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CHEMICAL INDUSTRY AND SCIENCE OF THE USSR

ON THE 40TH ANNIVERSARY OF THE GREAT OCTOBER SOCIALIST REVOLUTION

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Today chemical science and chemical industry have become one of the driving forces in the development of prosperity. It is therefore perfectly natural that great attention is being paid to the expansion of chemical science and industry throughout the world, including our own country.

Chemistry is one of the sciences that attained a high level of development even in prerevolutionary Russia. Great Russian scientists figure among the celebrated chemists of the past. This level was in no way paralled, however, by the chemical industry. This fact was a hindrance to the solution of the great problem of utilization of natural resources and to the development of the productive resources of the country immediately after the Great October Revolution.

Prerevolutionary Russia occupied the fifth place among the main industrial countries of the world and processed about 2-3% of the world's industrial output. Processing of chemical products, however, was on a relatively smaller scale. In 1913 Russia produced 121,000 tons of sulfuric acid, 51,100 tons of caustic soda, 160,000 tons of calcined soda, 69,000 tons of inorganic fertilizers, 1,520,000 tons of cement, and 4,443,000 tons of coke. Many of the most important chemicals were not manufactured at all or only in very small quantities. After the revolution it was necessary to virtually build up the chemical industry almost entirely again.

By 1927 or 1928 the rehabilitation of the chemical industry had been completed and outputs of chemical products exceeded the 1913 level. Since 1928 a large number of chemical plants and metallurgical chemical undertakings have been constructed; these included reconstructed and expanded older plants. The mineral fertilizer industry may be cited as a typical example of the development of chemical industry in the USSR as a whole. Prior to the revolution the annual production of the few superphosphate and phosphorite plants, mainly on the basis of imported phosphorites, was only about 60,000 tons. Nitrogen and potash fertilizers were not produced at all in old Russia apart from small quantities of ammonium sulfate from coking plants.

Large superphosphate-manufacturing plants were built in Russia in the thirties and later. Many deposits of phosphate rock were discovered, investigated and exploited. The most important of these are the apatite deposits in the Khibinsk Mountains on the Kola Peninsula and the phosphorites of Kara-Tau in the Kazak SSR. Numerous "local" deposits of phosphorites were also discovered and partially exploited in various regions of the USSR — Egorev, Vyatkov, Shchigrov, Esthonia, Aktyubinsk, etc. An outstanding event was the discovery in 1925-1926 of substantially inexhaustible deposits of potash salts (sylvinite and carnallite) in the Northern Urals at Solikamsk and Berezniki which formed the basis of an important potash fertilizer industry. Large synthetic ammonia and nitrogen fertilizer plants were built in various regions — Central Russia, Urals, Ukraine, West Siberia, Uzbekistan and the Transcaucasian Republics. In 1940 the output of inorganic fertilizers (phosphate, potash and nitrogen) exceeded 3 million tons, while in 1956 it amounted to 10.9 million tons.

Various other branches of chemical industry were developed at the same time: inorganic acids, caustic alkalies, salts, plastic masses, organic dyes, lacquers and paints, synthetic rubber, synthetic fibers, synthetic ethanol, products of basic organic synthesis, toxic chemicals for agriculture, chlorine and its organic derivatives, etc. Vast plants were erected for the coke-chemical industry, the chemical processing of petroleum, the production of cement, ceramics (including refractory types), domestic and electrotechnical porcelain, different types of glass, etc.

In 1956 the USSR produced 4.3 million tons of sulfuric acid, 631,000 tons of caustic soda, 1,545,000 tons of calcined soda, 77,000 tons of organic dyes, and 24.9 million tons of cement. Output of coke was 46.6 million tons with a corresponding expansion of the coke-chemical industry. The tempo of development of the chemical industry of the USSR increased.

In 1956 the over-all production of industry in the USSR was more than 30 times that of 1913, but the over-all production of the chemical industry had increased more than 100 times in the same period. The industrialization of the USSR had progressed to such an extent that it was second only to the USA among the industrial countries of the world. Today the USSR is responsible for about 20% of the world's industrial output. In respect to the chemical industry the USSR likewise occupies the second place in the world, although the difference in absolute output of many chemical products in relation to the USA is still considerable.

The building-up of the chemical and allied industries required a well-established chemical machine industry. Specialized works were built in Central Russia, Ukraine, Urals, Siberia and other regions for the fabrication of pumps, compressors, cooling installations, chemical apparatus, controlling and metering instruments, automatic devices, and other essential equipment.

The Sixth Five-Year Plan for development of the national economy of the USSR envisages further growth of the chemical industry at an increased tempo. It is planned to bring production of mineral fertilizers to 19.6 million tons in 1960, that of calcined soda to 2.42 million tons, that of caustic soda to 1 million tons, that of artificial and synthetic fibers to 330,000 tons, and that of cement to 55 million tons. One of the most important tasks of the chemical industry in the Sixth Five-Year Plan is to secure a considerable increase in utilization of refinery gases and natural gases and of petroleum products for the manufacture of synthetic rubber, ammonia, alcohols, engine fuels and other chemical products with the aim of a considerable reduction in the consumption of edible raw materials for these purposes. At the same time a very large expansion of the chemical machine-constructing industry is envisaged. The output of chemical equipment in 1960 is fixed at 208,000 tons or 184% more than in 1955. The plan for development of the chemical industry is associated with a proportional expansion of the power resources. Production of electric power is planned to be expanded by 188% over the 1955 level,and 320,000 million kilowatt-hours should be generated in 1960 as against only 1,900 million kilowatt-hours in 1913.

Chemical science has rendered great service in the development of the chemical industry. Since the first days of the existence of the Soviet State,enormous importance has been attached to the development of science in Russia and to its participation in the national economy. Establishment of a large network of scientific research institutes and higher educational institutions was put in hand, and these later played a prominent part in the development of science and the industrialization of the country.

Among the chemical research institutes that were founded shortly after the October Revolution were the Karpov Institute of Physical Chemistry (1918), the Scientific Research Institute for Fertilizers and Insectofungicides (1919), and the State Institute of Applied Chemistry (1920). These were followed by: the State Institute of the Nitrogen Industry, the All-Union Scientific Research Institute of Mineral Raw Materials (VIMS), the Scientific Research Institute for Organic Intermediates and Dyes, and institutes for reagents, synthetic rubber, rubber industry, tire industry, plastic masses, synthetic alcohols, synthetic fibers, metallurgical chemistry, soda industry, surface coatings industry, glass, glass fiber, cement, constructional and electrotechnical ceramics, chemical machine construction, oxygen production, etc., as well as a series of institutes for the planning of chemical projects, and a large network of works laboratories.

A large number of chemical research institutes and laboratories are now in being not only in the chemical industry but also in neighboring fields: petroleum, food, textiles, coal, aviation, building materials, radiotechnics, metallurgy, sanitation, agriculture, transport, communications, etc. Industrial research institutes and laboratories mainly solve problems associated with the maintenance of routine production, but they also concern themselves with the improvement of processes and the development of new technological processes and equipment; in many of them important theoretical problems are also studied. The solution of general scientific and theoretical problems of chemistry and chemical technology is the main function of the chemical laboratories and institutes of the Academy of Sciences of the USSR and of the academies of the Soviet Republics which were mainly established likewise in the post-revolutionary period. Numerous investigations by the chemical researchers of our country have not only enriched and advanced the sciences but have also exercised an important influence on the growth of chemical industry.

On the basis of physicochemical analysis, Academician N. S. Kurnakov and his co-workers have made a creative contribution of the development of the chemistry and technology of natural salts and metallic alloys. Their investigations have been utilized in the establishment in the USSR of the manufacture of potash and magnesium salts, sulfates, etc. and of a number of alloys. The investigations of E. V. Britske, D. N. Pryanishnikov, A. E. Fersman, P. I. Preobrazhensky and others have played a large part in the creation in the USSR of the inorganic fertilizer industry and of its raw material basis. The work of P. P. Shorygin and his school has influenced the development of the synthetic fiber industry and the chemical processing of cellulose.

The scientific investigations of M. I. Ilinsky, A. E. Porai-Koshits, N. N. Vorozhtsov and their co-workers have largely contributed to the development of the industry of organic intermediates and dyes and other complex organic substances. The work of A. E. Chichibabin, A. P. Orekhov, V. M. Rodionov and others has substantially contributed toward the growth of the pharmaceutical chemical industry. The outstanding researches of A. N. Bakh and his school have served as a basis for creation of the vitamin industry and for the initiation of numerous biochemical processes.

An enormous debt is owed to N. D. Zelinsky and his great school, to S. S. Nametkin and to many others for the development of processes for the large-scale chemical treatment of petroleum. Soviet scientists have had a great influence upon the development of the plastics and synthetic rubber industries by their work in the field of synthesis of high-molecular materials and their study of the influence of the structure of the raw materials on polymer properties.

Development of a method of synthesis of organosilicon polymers in the USSR has revealed new bases for manufacture of high-temperature-resistant oils, rubbers and electrical insulants which constitute a new branch of chemical industry. Important progress has been made in the investigation of telomerization reactions which are having a fundamental influence upon the development of the synthetic fiber industry. Studies of A. E. Favorsky and his school have laid the foundations for an acetylenic chemicals industry involving the synthesis of very important organic substances.

Great successes have been scored in the field of silicate chemistry and technology, leading to the production of new types of binders, radiotechnical ceramics, highly refractory materials, etc. (work of A. A. Baikov, I. V. Grebenshchikov and others).

In the Soviet Union a theory has been developed in connection with chain-branching reactions which is the basis of industrial processes of combustion, oxidation, detonation, chlorination, polymerization and others. The author of this theory, Academician N. N. Semenov, was awarded the Nobel prize for chemistry in 1956 jointly with the English scientist Hinshelwood. The study of the mechanism of chain reactions has been greatly aided by new methods, notably mass spectroscopy and paramagnetic resonance (developed by E. K. Zavoisky), as well as by a new kinetic method of empolyment of labeled atoms.

Many scientists and chemical engineers in the Soviet Union are actively participating in the solution of a series of vital problems of nuclear physics and the peaceful use of atomic energy, as well as of rocket technology. Soviet scientists have solved many other important technological problems, some examples of which are mentioned below in relation to processes developed and brought into use for the first time in our country.

The celebrated researches of S. V. Lebedev and his school had great theoretical and practical value in the solution of the synthetic rubber problem; in 1928 they worked out an industrial method of production of butadiene from alcohol and its polymerization. In July 1932 in the Soviet Union the first large synthetic rubber plant in the world was started up. The factory was equipped with apparatus of original types designed and fabricated under the supervision of young Soviet chemical engineers. Several large synthetic plants are now successfully operating the Lebedev process. Copolymerization of butadiene with other components provides a wide range of industrial rubbers with various physicochemical and mechanical properties.

Very valuable work has been carried out on the synthesis of isoprene rubber with regular structure, approximating to natural rubber in its main properties. Students and disciples of S. V. Lebedev developed two industrial processes for preparation of very pure isoprene. One of the processes is a two-stage one. In the first stage isobutylene and formaldehyde yield dimethyldioxan which in the second stage is catalytically converted into isoprene. The second method involves catalytic dehydrogenation of isopentane to isoprene.

P. G. Sergeev and R. Yu. Udris with co-workers carried out successful investigations on a fundamentally new route to phenol. Studies on the oxidation of isopropylbenzene, commenced in 1939, led to an elegant and technically adequate scheme for preparation of phenol: isopropylbenzene, obtained by alkylation of benzene with isopropylene, is oxidized with atmospheric oxygen to form the hydroperoxide which on decomposition yields acetone and phenol. Large-scale production of phenol by this method started in 1949. This method affords the possibility of manufacture of other hydroxy derivatives of the aromatic series and of ketones of very great importance.

Very valuable work has been carried out on the synthesis of methylstyrene. In 1943 R. Yu. Udris discovered an interesting reaction for cleavage of isopropylbenzene (cumene) hydroperoxide with formation of dimethylphenyl carbinol. The technology and equipment for the process were developed by a group of chemical engineers under the direction of the chief authors. The technical difficulties had been overcome by 1953.

The necessity for manufacture of ethyl alcohol (the main raw material for synthetic rubber) by the most economical process was appreciated by investigators even in 1930-32. Fundamental studies in this field led to the establishment of a method of direct hydration of ethylene to ethyl alcohol. The raw material for this process was 97-98% ethylene supplied by the petroleum refineries. The factories constructed and operated in the USSR convincingly demonstrate the advantage of this process over other processes for ethyl alcohol.

Attention should be drawn to the important studies on the production of aniline by catalytic reduction of nitrobenzene carried out by the Institute of Research on Intermediates and Dyes. These studies led to a solution of the problem of catalytic reduction of nitrobenzene with hydrogen in the gas phase. The same institute developed a commercial method of oxidation of naphthalene to phthalic anhydride over a powdered catalyst in a fluidized bed and carried out the design of the catalytic plant for this purpose. This method of production of phthalic anhydride affords the possibility of constructing high-capacity units of simple design which can be automatically controlled at all stages of the process.

The State Institute of the Nitrogen Industry developed and brought to the industrial scale a process of gasification of low-grade fuels (lignites, peat, etc.) in a fluidized-bed gas producer of high productive capacity with the help of oxygen-enriched air. The first industrial unit (GIAP-1) for the gasification of a finely granular fraction (0-12 mm) of coal came into operation in February 1950 at the Chirchik Electrochemical Combine. At the present time, new gas producers are being used for industrial gas manufacture in a number of new plants in the USSR, Bulgaria and the Chinese People's Republic.

A process for roasting of pyrite in the suspended state and in furnaces with a "turbulent layer" was developed and brought to the technical scale by the Scientific Research Institute for Fertilizers and Insectofungicides. The output capacity of these furnaces when operating on pulverized pyrite is over ten times that of mechanical shelved furnaces. The degree of combusion of the sulfur is 98.9-99%. At the same time each ton of pyrite produced 1.1-1.2 tons of steam at a pressure of up to 6 atmos. Operation of the furnaces is completely automatic, and substantially no physical effort is exerted by the staff of workers. This process is especially important for the USSR because pyrite, mainly in the form of flotation tailings from concentration plants of copper works, is the principal raw material for the manufacture of sulfuric acid. Furnaces with "turbulent beds" are finding ever more extensive application in the roasting of zinc concentrates. Over 50% of all the zinc concentrates processed at zinc works in the Soviet Union are now roasted by the turbulent bed method.

Engineers of the Karagandin coal basin have developed, and successfully launched on the industrial scale, a method of enrichment of coal with the help of a friable, finely granular material fluidized with air. The new method of classification of lumpy materials on the basis of specific gravity has great potentialities in other branches of the mineral industry.

Shortly before the second world war work was started at the Mendeleev Moscow Institute of Chemical Technology on the production of foamed glass which culminated in the creation of an industrial process for the manufacture of this new type of building material. This has a low specific gravity and good thermal insulating and sound-deadening properties. In the years 1948 to 1951 a technique was worked out for the production of an ultra-strong stone on the basis of finely pulverized corundum. This material is now manufactured on the industrial scale and is employed for the fabrication of a cutting tool for cold-working of metals, and also for the fabrication of various tools used under conditions calling for high resistance to grinding action.

A method has been evolved for the production of strong building materials on the basis of plastic masses reinforced with fine, plane-parallel glass fibers in the stressed condition.

Enormous qualitative as well as quantitative changes have taken place in recent decades in the chemical industry. Factories of the chemical industry are characterized by a great diversity of the most complex techniques, automatization of production, replacement of batch processes by high output continuous processes, extensive application of catalysis in the production of inorganic and organic products, development of a highly efficient system of internal transport involving a diversity of material-handling methods, etc.

In this connection, chemical technology as a science has acquired a new content; instead of being empirical it has itself become a science in the shape of a synthesis of engineering disciplines based on the firm foundation of chemistry, physics and mathematics. The hard core of chemical technology as a science is the knowledge of the main processes and installations of chemical plants and the general laws of technological processes. This science began to acquire its present form and importance under the pressure of industrial necessities in the twenties of this century in a number of countries. The foundations of this science were laid in Russia in prerevolutionary years by famous engineering scientists: by A. K. Krupsky at the Petersburg Institute of Technology and by I. A. Tishchenko at the Moscow Higher Institute of Technology. This science began to develop with exceptional speed in our land after the October Revolution.

Scientific research on the most important processes of chemical technology has developed on an extensive front in the USSR since the start of our industrialization and especially in the period after the second world war: absorption, adsorption, rectification, extraction, molecular distillation, ion exchange, drying, filtration, crystallization, mixing, flotation, etc. New types of chemical plants)have also been evolved. A great deal of this work is carried out in the laboratories of higher educational institutes.

Development of chemical science and industry is inconceivable without the training of an ever increasing number of highly qualified engineers and scientists. The differences between chemical science and industry on the one hand and the reciprocal influence of the separate branches of industry on the other hand necessitate the training of variously specialized chemists on a very broad theoretical foundation. This principle is reflected in the system of higher education of the USSR.

Energetic measures for development of higher education were taken since the first years of existence of the Soviet State with the objective of creating considerable cadres of intelligentsia in various branches of knowledge. Higher education has made enormous progress in our country. Prominent among the specialists educated by the Soviet system are chemical engineers and chemists trained at university level. In prerevolutionary Russia only a few hundred chemists had received a higher education. In postrevolutionary Russia the number of chemists with higher education runs into tens of thousands. Russian university training of chemical engineers and mechanical engineers for the chemical and allied branches of industry in the main meets the requirements of chemical science and industry.

Soviet chemists and engineers greet the fortieth anniversary of Great October with a feeling of tremendous pride in the progress of our land, in the achievements of our chemical science and industry. At the same time, they cannot forget that the output of many chemical products is still a long way from satisfying the country's needs and that there are still serious deficiencies in some branches of chemical science.

On this anniversary of the foundation of our socialist state, Soviet chemists are fully resolved to bend all their energies toward fulfillment of the resolutions of the 20th Congress of the Communist Party of the Soviet Union, and to increasing their contribution towards the most rapid development of chemical science and industry.

SOME RESULTS OF THE DEVELOPMENT OF PHYSICOCHEMICAL MECHANICS

P. A. Rebinder

Report to the Session of the Division of Chemical Sciences of the Academy of Sciences of the USSR,

October 31, 1957

During the past ten years a new field of physicochemical science has made its appearance (mainly on the basis of work by Soviet scientists) which is on the border between physical and colloidal chemistry, the molecular physics of the solid state and the mechanics of materials. The main objectives of this new branch of knowledge [1] are: 1) to establish the laws and mechanism of formation of solids with a given structure and given mechanical properties; 2) to study the mechanism of the processes of deformation and fracture of solids with reference to the influence of physicochemical factors (composition and structure of the substance, temperature and medium) in order to determine the optimum conditions for mechanical working of different types of solids by compression, cutting and fine grinding.

The development of physicochemical mechanics is accordingly associated with two groups of new problems of importance in modern colloid chemistry (or more correctly the physical chemistry of disperse systems and surface phenomena: 1) problems of structure formation [2], i. e., development of spatial structure by random linking of molecules in a liquid medium with maintenance of thin films between them by growth of crystallites or development of a polymer network; 2) problems of dispersion of solids (development of new surfaces during deformation and breakdown) [1]. These two fundamental groups of problems of colloid chemistry are closely interlinked: on the one hand the mechanical properties of solids and the structural systems intermediate between solids and liquids are governed by the nature of the structures developed in them; on the other hand the process of structure formation in some cases can only take place when the solid phase is highly dispersed, and this is effected by efficient dispersion in a surface-active medium. Examples of such processes are the coagulative, thixotropic structure-forming changes during sol−gel transformations which are so characteristic of colloidal two-phase systems whose degree of dispersion has reached its limit. We see that physicochemical mechanics involves problems of rheology, i. e., the investigation of the kinetics of development of deformations and of relaxation processes in structure-forming systems and solids, but these are by no means the only examples of such problems. The main function of physicochemical mechanics from the practical aspect is to serve as a foundation for the production of constructional materials (concretes and alloys) with specific mechanical properties and structures.

In connection with the two branches of physicochemical mechanics mentioned above (structure formation on the one hand and processes of deformation and breakdown on the other), we shall now examine some results obtained in recent years by the Division of Disperse Systems of the Institute of Physical Chemistry of the Academy of Sciences, USSR and in the Department of Colloid Chemistry of Moscow University.

Our researches with Segalova and Serb-Serbina [2-6] showed that we must distinguish between two types of three-dimensional structures: coagulated and condensed-crystalline structures. In coagulated structures the particles of the disperse phase are associated in a random network such that thin films of the liquid medium remain along the microsurfaces of contact. Such structures consequently possess relatively low stability as well as very marked plasticity (capacity for extremely large residual deformations without breakdown). Independently of the nature of the solid particles constituting these structures, they manifest (as we showed) a striking susceptibility to slow elastic deformations; the resultant residual elasticity is characteristic of systems passing into elastomers such as rubbers and their solutions. Coagulative structures are also completely thixotropic, i. e., they spontaneously regain their original rigidity after mechanical breakdown due to gradual development of a framework

favorable to collisions of particles in brownian movement, as we demonstrated with diverse systems (colloidal suspensions of calcium stearate in hydrocarbons, bentonite clays in water, hydrosols of alumina and vanadium pentoxide).

In contrast to the coagulative structures, condensed-crystalline structures are developed under the action of very strong linking forces, i. e., main chemical valences as in the formation of three-dimensional polymers, for example, in silicic acid gels or vulcanized linear polymers. Extremely long crystalline structures are formed by direct growth of crystallites of a solid phase originating from a supersaturated solution or a supercooled melt or by sintering of solid particles ("cement stone," pure metals and alloys, ceramics and metalloceramics). These structures possess maximum toughness, and are characterized by brittle fracture, lack of residual deformation, and complete absence of thixotropic properties (they break down irreversibly). The plasticity or elasticity of such highly rigid structures is caused by the properties of the components of the structure, i. e., crystallites or macromolecules. The plasticity of metals, for example, is highest in single crystals; similar considerations account for the elasticity of rubber vulcanizates and silicic acid gels. We showed that these gels are entirely nonthixotropic and give elastic-brittle fracture, i. e., they are incapable of true flow (the latter must not be confused with very slow but fully reversible, i. e., highly elastic, deformation). In harmony with this view, Kargin and Slonimsky have recently shown that true flow, i. e., formation of residual deformations in three-dimensional polymers, can only be a chemical process — the consequence of local breakdown and recombination of segments of chains which are already in the deformed state.

The strength of crystallized structures, i. e., polycrystalline solids, is governed, for a given crystal lattice made up of different elements of structure, by their dimensions (dispersity), a degree of disorientation, conditions of growth, and porosity. It thus becomes possible over a wide range to control the mechanical properties of the resultant structures at various stages of their development by means of adsorbent additives or by varying the conditions of formation of the new phase (degree of supersaturation). The theory of structure formation constitutes the scientific basis of production of high-quality solid materials, such as concretes (by hydraulic hardening of cements), bitumens, plastics and rubbers with active fillers, and a variety of alloys.

Coagulative and condensed-crystalline structures are broadly interrelated; they can pass from one into the other under certain conditions: by mechanical breakdown (dispersion of the crystallized structures, especially in a medium in relation to which they are sufficiently lyophilic, e. g., soaps in water or in hydrocarbon liquids) or by degradation of the crystalline structure, a thixotropic coagulated structure is formed which we therefore sometimes call a dispersed structure. This corresponds to the abrupt fall in strength on initial fracture with complete reversibility of restoration of thixotropic rigidity after subsequent fractures. Crystallized structures can also be formed on solidification of mineral binders due to binding of relatively larger particles by crystallites of the primary coagulated structure growing from the surrounding medium. Finally, on gradual careful drying of coagulated structures of maximum density, the particles approach the regions of contact and the system gradually approximates to a crystalline structure as in the genesis of sedimentary rocks. The concept of two forms of structure formation constitutes the basis of a theory of hardening of hydraulic binders (lime, gypsum, cement) and is accordingly the physicochemical basis for the development of a theory of concretes.

The characteristic features of coagulated structures may be illustrated by two examples [2, 3]:

1. It is well known that typically thixotropic suspensions of bentonite clays change in course of time into the thixotropic gel state due to development of a plastic, solid three-dimensional network. In suspensions of maximum structural strength an elastic region is observed bounded by the yield point, while under high stresses we find steady flow in the case of a degraded structure with a different degree of breakdown in flow. Since in the case of thixotropic structures we must always assume the presence of thin residual films of liquid medium between the linked particles, we can assume that even with the smallest shearing stresses below the yield point, i. e., in the elastic region, slow flow of the creep type ought to be observed in the structure of maximum strength; this type of flow remains undetected in normal experiments due to the extremely high viscosity. It was actually detected in precision measurements by Abduragimova [6] in our laboratory, using a torsion apparatus of the Shvedov type, in a narrow gap between coaxial cylinders. The final result is plotted in Fig. 1 as the dependence of effective viscosity on the shear stress maintaining steady flow. We see that on transition from larger to ever smaller shear stresses (each time awaiting establishment of the maximum structural strength), there is observed a continuous rise in viscosity from the smallest limiting value (corresponding to the maximum breakdown of the flowing structure at the limit) up to substantially infinity at a stress of $P_k = 25$ dynes $\cdot$ cm^{-2}, which determines the practical
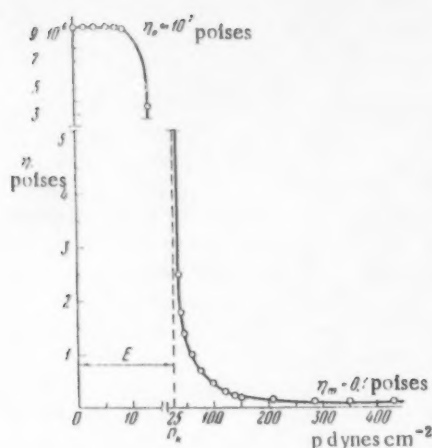
Fig. 1. Dependence of the effective viscosity $\eta = P/\frac{d\epsilon}{d\tau}$ on the shearing stress P under conditions of uniform movement in a steady flow ($\frac{d\epsilon}{d\tau}$ is the rate of flow) for a thixotropic coagulated structure at the strength limit (10% suspension of Oglanlin bentonite in water); t = 20°C.

yield point (elastic limit). On passing to stresses below the limit the viscosity increases abruptly by a power of 8 and becomes constant at the limit of $\sim 10^7$ poises. In this quasielastic region, flow takes place in the substantially unmodified structure.

2. In equilibrium, thermodynamically stable, semicolloidal solutions, such as aqueous solutions of saponaceous surface-active substances, the equilibrium distribution curve is continuously displaced towards larger micelles (ultramicrocrystallites) with rising concentration or falling temperature. This process is accompanied by development of a three-dimensional gel structure. We thus obtain the transition: true solution $\rightarrow$ sol $\rightarrow$ gel. An effect similar to that of changes of temperature and concentration is secured with additives which coagulate or peptize micelles. As we know, the phenomenon of solubilization is observed in such systems — the solution of hydrocarbons in soap micelles (induced or colloidal solubility). Our investigations have shown that the formation of a three-dimensional gel structure on increase of concentration of the saponaceous semicolloid is associated with change of type of the micelles formed, and therefore leads to an increase in the specific induced solubility (in moles of hydrocarbon per mole of soap) when the gel structure is developed [7]. In relatively dilute solutions, but

above the critical concentration of micelle formation, spheroidal micelles appear whose structure corresponds to the minimum free surface energy and comprises a nucleus of hydrocarbon chains and an outer hydrated shell of polar groups. More than 20 years ago Hartley and I (independently) introduced the concepts of such spheroidal micelles. On increase of the concentration of soap (sodium oleate) to 0.33 mole/liter, the highest limiting viscosity η_0 increases only 10 times to 0.1 poise (at 20°), and in this region the specific solubilization remains constant. But on further increase of the concentration of soap to 0.53 mole/liter, η_0 rises to 100 poises, i. e., by a factor of 1000, while at a concentration of 0.8 mole/liter the viscosity rises to 10 poises. At the same time the spheroidal micelles are progressively transformed into lamellar forms, and these facilitate the development of a three-dimensional structure, a process which is accompanied by increased specific solubilization of hydrocarbons. The influence of additions of these solubilizing substances on the structural-mechanical properties of a soap gel is interesting. Thus, according to the experiments of Markina [7] the introduction into a solution of sodium oleate (0.8 mole/liter) of 0.22 mole of dodecane per mole of soap lowers the limiting viscosity by a factor of 200,000 from 10^4 to 0.05 poises; swelling of the lamellar micelles by absorption of hydrocarbon causes these micelles to become spheroidal micelles similar to droplets of a stabilized hydrocarbon emulsion in water. Such ultramicrodroplets are protected against coagulative agglomeration by the hydrophilic shells which leads to abrupt fluidization of the structure, i. e., to a gel $\rightarrow$ sol transition, and to equivalent considerable dilution of the soap solution.

Additions of polar, surface-active substances with shorter hydrocarbon chains, which themselves do not form micelles and three-dimensional structures in aqueous solution, have an opposing action: marked strengthening of the gel structure of the soap due to formation of supplementary bonds; e. g., the addition of 0.08 mole of octyl alcohol to 1 mole of soap raises the limiting viscosity by a factor of thousands (over 10^7 poises) and develops a distinctly solid gel structure. These examples clearly demonstrate the possibility of regulation of the structure formed and of its mechanical properties by means of additives of various types.

Passing on to the region of crystallized structures, we shall limit ourselves to consideration of the most interesting case of structures of solids — that of the finely crystalline concretion formed when a new phase crystallizes out of a supersaturated solution within an original coagulated structure of solid particles mixed with water in the form of a paste (a suspension of maximum concentration). Such crystallized structures are developed in

building mortars or concrete mixes on the basis of inorganic binders such as lime, gypsum and cements in the processes of hydraulic hardening [8-10]. Examination of the over-all balance of the chemical transformation shows that the process of hydration of the binders mentioned resolves itself (as we now know) into a gradual dissolution of the whole of the originally dispersed binder and crystallization of a new hydrate form from the supersaturated solution. In this connection we must not forget the important initiating role (as we may call it) of the adsorptive interaction of water with the exposed surfaces in the surface defects of the crystal lattices of the binders (unquenched lime, gypsum hemihydrate, mineral clinkers like tricalcium aluminate). These processes can be the initial stage of dissolution, i. e., of formation of a solution supersaturated with respect to the new hydrate form developed as not very fine crystallites [10-13].

On the other hand, both coagulative and crystallized structure formation can be controlled at the initial stage of the setting process by the joint effect of additions of surface-active substances (various types of plasticizers) and mechanical action (vibrating treatment) which causes activation of the binder, breakdown and maximum densification of structure. The combined effect of these two types of factors (mechanical and adsorptive) is the basis of Mikhailov's scheme for production of hard and rapid-setting concrete mixes for high-grade, strong and enduring structures, especially for factories making concrete and reinforced concrete structural components [14].

The effects of adsorptive additives (surface-active plasticizers) can be broadly classified under two main headings:

1. Stabilization of a suspension of particles of the primary binder and development of crystallites of new forms, i. e., the prevention of development of coagulated structure, and aging retardation of crystallites of the new hydrate form. Such a stabilizing action of plasticizing additives, while sharply lowering the strength of the initial structures, affords the possibility of maximum densification even by relatively weak mechanical action.

2. When adsorbed onto the primary particles of binder, surface-active additives can retard the process of their solution. But when adsorbed onto the fresh nuclei of crystallization of the new phase, the surface-active additives slow down the growth of the crystallites and the increase of strength of the crystallized structure in the initial stage, thus promoting the further formation of a more finely granular crystalline structure of the cement in concretes (adsorptive modification of crystallization).

Both of these groups of effects facilitate the solution of the main problem of modern concrete technology — the creation of a sufficiently prolonged induction period of the setting process during preparation of the concrete mix and its introduction into the form or mold;   during this period the dispersed mix should retain its plasticity (mobility), so that after completion of charging into the form the final process of setting should proceed to completion at maximum speed in a structure of maximum density. While the effects of the first group (stabilizing effect or lowering of the strength of the coagulated structure) can be replaced by mechanical (vibrating) action of suitable intensity which destroys the structure developed during the initial stage, the effects of the second group (adsorptive retardation of the development of crystalline structure during the initial stage) cannot obviously be replaced by mechanical effects. Best results will be achieved by combined application of optimum mechanical action and optimum additions of surface-active plasticizers. The latter enable a considerable reduction of intensity of the optimum mechanical action, while intensive vibration or vibrocompression in turn changes the conditions of action of adsorptive additives and permits the utilization of a very much wider range of such agents, e. g., ranging from hydrophilic to hydrophobic plasticizers.

Segalova, Lukyanova, Izmailova and Solovyeva [10, 12, 13] have studied the characteristics of the development of crystalline structures during the setting of hydrated binders. These characteristics can be illustrated by the simplest example of setting of calcium sulfate hemihydrate in concentrated aqueous suspensions (Figs. 2 and 3).

Figure 2 shows the occurrence of an appreciable induction period corresponding to the coagulated structure, on whose basis is later developed the crystalline structure which loses the ability to undergo reversible regeneration after destruction (grinding) in the subsequent stages of development. Maximum strength is attained at the same time on complete hydration, i. e., transformation of the whole of the calcium sulfate hemihydrate by crystallization from a supersaturated solution to form calcium sulfate dihydrate which is the final composition. The picture of the kinetics of development of the strength of the crystallized structure and its regenerative capacity after grinding is in complete harmony with the data from colorimetric studies of the kinetics of supersaturation of relatively dilute suspensions of calcium sulfate dihydrate. We see that maximum supersaturation (rapidly developed)
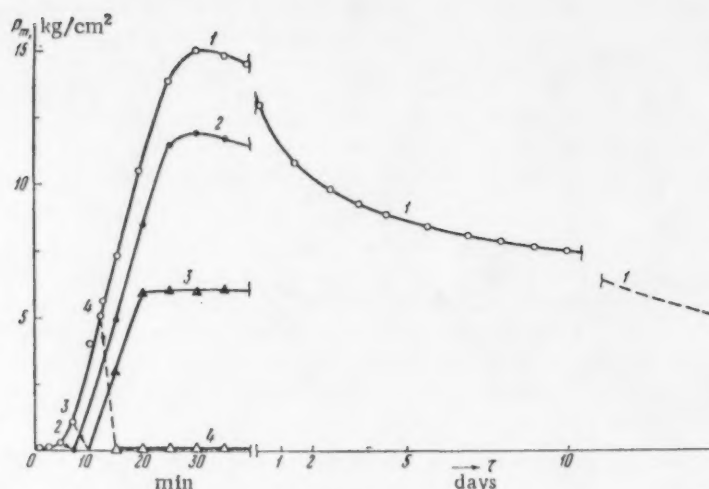
Fig. 2. Kinetics of growth of plastic strength (P_m) of structure in gypsum plaster
from 30 g $CaSO_4 \cdot 0.5\,H_2O$ + 70 g pure, ground quartz sand + 50 g water (B/T = 0.5):
1) undestroyed structure (triturated on mixing for 1-3 min); 2) structure destroyed
(further grinding for 2 min) after 5 min; 3) the same after 7 min; 4) the same after
12 min. The strength of the original coagulated structure was ≈ 1-10 g/cm²; the
maximum strength of the crystallized structure after 30 min (period of complete
transformation into $CaSO_4 \cdot 2H_2O$) ≈ 15,000 g/cm².

is maintained in the aqueous medium of the suspension until the rate of input of ions due to solution of the primary
solid phase compensates for the rate of removal of these ions from solution due to the newly formed hydrated modi-
fication crystallizing out. Increased content of the disperse solid phase (the initial binder in suspension) does not
alter the upper limit of supersaturation but only accelerates its subsequent diminution.

Figure 3 demonstrates the remarkably interesting influence of increasing additions of prepared highly dis-
persed dihydrate on the kinetics of supersaturation as well as on the development of the strength of the crystallized
structure. Introduction of such conditions enables us to clarify the mechanism of growth of strength in the crystal-
lized structure. Here the main part is played by coalescence of the new crystallites which becomes possible only
when growth is sufficiently fast, i. e., under conditions of high supersaturations. On introduction of fairly consider-
able quantities of new formations, the attainment of any considerable degree of supersaturation cannot occur due
to the high speed of crystallization. That is precisely why grinding of the pastes from ordinary calcium sulfate
hemihydrate does not lead to further growth of strength (i. e., development of a crystallized structure) without
any additives (as in Fig. 2) and when hydration is still a long way from completion (i. e., much insoluble binder
is still present). Under such conditions dihydrate continues to crystallize out from solution onto the surface of the
new formations which are already present in large quantities; this results in formation of well-developed crystals
of calcium sulfate dihydrate (approaching thermodynamical equilibrium) but which are not at all coalesced, re-
sulting in a hundredfold reduction of final strength. It is also evident from Fig. 2 that further prolonged main-
tenance of the completely hardened crystallized structure of calcium sulfate dihydrate leads, under conditions
of equilibrium of the water vapor pressure (i. e., when there is no loss of water) to gradual and continuous fall in
strength possibly with ultimate complete wetting. Observations under the microscope show that this effect is irre-
versible and is bound up with gradual recrystallization through the solution filling the pores of the gypsum plaster,
thermodynamically unstable surfaces of intergrowth with the unavoidably deformed crystal lattice, with formation
of crystallites of dihydrate thermodynamically closer to equilibrium and not bound to one another. This gradual
and spontaneous loss of strength accordingly does not resolve itself into adsorptive reduction of strength and does
involve creep of the gypsum as observed by Logginov in our laboratory. Unlike the effects of recrystallization of
contacts, the effects of adsorptive lowering of strength are fully reversible on drying and arise rapidly after moisten-
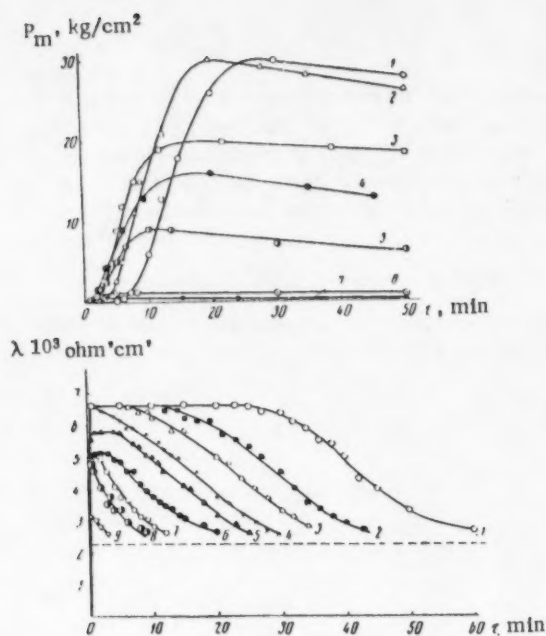
Fig. 3. Lower graph: curve 1) kinetics of supersaturation on the basis of specific electrical conductivity in an aqueous medium on a suspension of 25 g $CaSO_4 \cdot$ $\cdot 0.5H_2O$ in 500 g water; curves 2-9) the same but with increasing additions of the product of hydration (calcium sulfate dihydrate): 2) 2g; 3) 10 g; 4) 20 g; 5) 25 g; 6) 50 g; 7) 75 g; 8) 100 g; 9) 200 g. Upper graph: kinetics of increase of plastic strength P of the corresponding pastes from 30 g $CaSO_4 \cdot 0.5H_2O$ + 70 g quartz sand + 50 g water in which increasing proportion of sand is replaced by calcium sulfate dihydrate:

Curves	1	2	3	4	5	6	7
Sand in g	70	68	65	60	50	20	0
$CaSO_4 \cdot 2H_2O$ in g	0	2	5	10	20	50	70

ing which does not of course require a long period since it is always associated with recrystallization in the structure.

The phenomena that we established of recrystallization associated with loss of strength are considerably weakened and almost completely disappear on passing to very much denser structures with smaller pore volumes filled with liquid (so-called aqueous or moist storage). These effects also become considerably weaker and are observed only after much longer periods of time in binders whose newly formed hydrates are considerably less soluble in water. Examples are aluminosilicate cements (portland cements) in which the ultimate strength of the crystallized structure is governed by hydrosilicate setting. On keeping in an aqueous medium, however, especially in the case of aluminate cements, such a recrystallization may be a very much more important cause of loss of strength then the usually considered corrosion of concrete and plaster. Physicochemical processes, which are closely associated with the very genesis of strength and with the formation of a new and finely crystalline phase, can here play a very much more important role than the generally known processes of ordinary chemical breakdown or solution.

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Our investigations long ago established [15, 16] that the resistance of solids to deformation and breakdown, their stability under the actions of stresses caused by external forces, is lowered by adsorption from the surrounding medium or adsorption of surface-active admixtures when the latter are sufficiently mobile within the structure of the solid. These phenomena are associated with lowering of the surface energy σ at the newly formed surfaces of defects of various types due to deformations, especially in the stages preceding breakdown. The effects of adsorption on strength and on the promotion of deformations bear a kinetic character and are associated with the promotion, i. e., with the increased probability of, development of surface micro- and ultramicrofissures and cracks, as well as with the initiation of slips in a given stressed state under the influence of adsorption.

Consequently, most of the adsorptive influences of the external medium are observed (as we showed) after prolonged action of favorable stressed states in the surface layers under conditions of creep and rupture under permanent or periodic loads (fatigue strength). When a solid is stressed in a surface-active medium it is even more necessary to keep in mind not only the strength (this is a largely undefined concept) but also the firmness or load-bearing capacity, i. e., the period of residence of the given solid in the loaded state before breakdown or development of considerable residual deformation. The firmness or load-bearing capacity is especially liable to be lowered by adsorptive interaction of the medium and additives. Consequently, adsorption can definitely induce qualitative change in the properties of a solid undergoing deformation.

The energy A and the probability W of development of slip centers or breakdown cracks at weak points in the deformed solid is governed, in analogy with the processes of formation of a new phase, by the magnitude of

the free energy at the interface (the surface tension σ at the interface with the surrounding medium):

$$A \approx \sigma \delta_m^2; \quad W \sim C \exp\left(-\frac{\sigma \delta_m^2}{kT}\right); \quad C \sim \exp\frac{\beta P \delta_m^3}{kT}.$$

In these approximate expressions, C is the intensity and character of the stressed conditions; P is the stress; β is a dimensionless factor relating also to the magnitude of the relative deformation for tensile stresses β > 0 and for compressive stresses β < 0; δ_m is the mean distance between the defects in solids — a measure of the ultra-microblocks associated with the markedly weakened bonding forces and corresponding to the mean size of the colloidal particles discharged into the surrounding medium under the action of thermal movement at a given temperature T. In the case of sufficiently small surface energies at the interface, i. e., in the case of sufficiently lyophilic systems, $\sigma < \sigma^* \sim \frac{kT}{\delta_m^2}$, the dispersion of a solid at weak points (defects) occurs spontaneously on introduction into a given medium in the absence of external mechanical effects under the influence of thermal movement alone (the case of bentonite in water or of iron in mercury with formation of an amalgam in the form
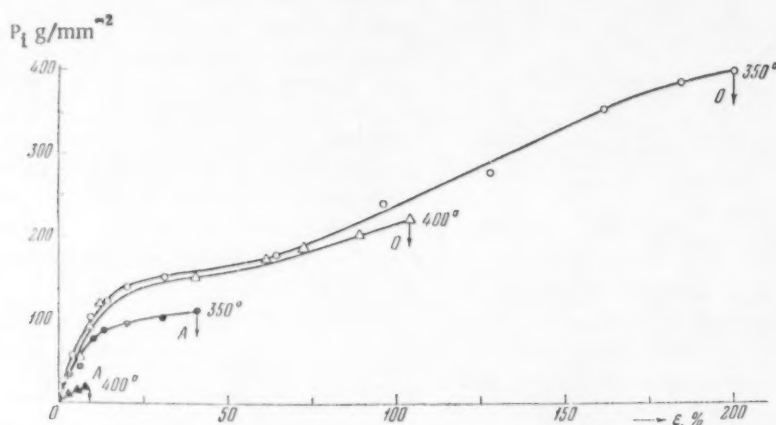
Fig. 4. Stress diagrams of zinc monocrystals: true stress $P_t = P_0 \left(1 + \frac{\epsilon}{100}\right)$, relative elongation $\epsilon = \frac{l - l_0}{l_0} \cdot 100\%$ at constant rate of elongation $\frac{d\epsilon}{d\tau} = 15\%$ min^{-1} at 350 and 400°. O denotes pure monocrystals of Zn (diameter 0.5 mm), Δ represents the same monocrystals coated with a thin film of tin (1-3μ). The arrow denotes rupture.

of colloidal suspensions or an iron mercurosol). In this connection the limit of spontaneous dispersion σ^* increases with rising temperature, and at room temperatures it is of the order of 0.1 erg/cm^2, while at high temperatures of the order of several thousand degrees it is still only of the order of 1 erg/cm^2. These data indicate more wide-spread existence than is usually assumed of stable pyrosols and thixotropic pyrogels formed in metallic and non-metallic melts at high temperatures. It must also be remembered that rise of temperature is accompanied by a sharp drop in the interfacial tension itself due to increased mutual solubility on approaching the critical point which corresponds to disappearance of the colloidal phase, i. e., unlimited reciprocal solubility with formation of a true (single-phase) solution. When $\sigma > \sigma^*$, dispersion cannot be spontaneous and it only takes place under the action of a stressed condition of sufficient intensity. The condition for mechanical breakdown in the simplest case when $\sigma\delta_m^2 \gg kT$ is expressed by $\sigma < \beta P \delta_m$.

We have made a detailed investigation of the adsorptive lowering of strength and of the promotion of de-formation of solids of various types under the influence of typical surface-active substances. However, the surface tension of solids is very much more strongly depressed by liquid fused agents similar to them in molecular struc-ture [20]. In the case of metals such agents are relatively low-melting metals and alloys; Kishkin and co-workers quite correctly [21] attribute the destructive effects of this type to an adsorptive effect (depression of surface energy), whereas formerly they had been thought*to result from intercrystalline corrosion.

* There appears to be some error in the reference to the literature cited. Kishkin and co-workers should read [20] ; Lichtman and Kichanova should read [21]. Whether there are errors in citations not accompanied by names is not known — Publisher's note.

Recent work in our laboratory by Likhtman and Kochanova [20]*established the occurrence of similar and extremely marked effects precisely on monocrystals possessing very high plasticity; they also observed the exceptional influence of the grain boundaries. Figure 4 illustrates the marked development of brittleness and the lowering of the strength by a factor of 10 or more due to the application of a thin film of tin to the surface of a zinc monocrystal at temperatures above the melting point of the zinc-tin eutectic. In the case, however, of extremely small tensile stresses (considerably below the yield point), the same coatings of surface-active metal were shown by Labzin (Department of Physics of Saratov Pedagogic Institute), in work carried out by him under the direction of Likhtman, to cause a sharp increase in the rate of plastic elongation (creep or microcreep) (Fig. 5).
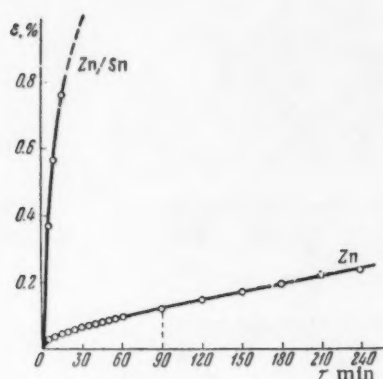

Fig. 5. Creep of microcrystals of zinc at t = 354° (diameter 1.0 mm, χ = 52°) (relative elongation ϵ% — time τ) under constant small tensile stress of P = 35 g/mm^{-2}; Zn is the pure monocrystal; Zn/Sn is the monocrystal covered with a thin film of tin (after experiments by Labzin).

The same effects of a sharp drop in strength and the development of brittleness were observed by Rozhansky and Pertsov [22] at room temperature on covering a zinc monocrystal or a tin monocrystal with a thin film ($\sim 0.1\mu$) of mercury. The film of mercury quickly became saturated with the underlying metal (mercury dissolves 2.2% of Zn and 0.6% of Sn at 20°). The interesting observation was here made that the destructive embrittlement of the amalgamated crystal completely disappeared at higher temperatures. In the fairly narrow temperature region of 120 to 160° a sharp transition from the brittle to the plastic state is observed (Fig. 6) with complete restoration of the plasticity and strength characteristic of a pure zinc monocrystal. At intermediate temperatures (130, 150°) the elongated crystal, which already exhibits considerable plastic elongation before rupture, is covered with a network of more or less deep but not completely intersecting cracks ("petals") round which the monocrystal is greatly strengthened, as evident from the small elongation (maintenance of width) at the sites of the cracks. These cracks become less and less frequent with rising temperature (Fig. 6) and disappear at 160° and higher. This effect is reversible (not associa-

ted with losses of mercury by evaporation), i. e., embrittlement and loss of strength occur afresh when the temperature falls to 100° or lower.

Lowering of the rate of deformation is found to have a similar effect to raising of the temperature in harmony with the experiments previously reported by Labzin on the creep of zinc monocrystals coated with tin.

Shchukin [22] showed how the observed abrupt transition from the brittle to the plastic state (i. e., restoration of plasticity) with rise of temperature could be explained on the basis of the modern theory of dislocations in crystals. Formation of cracks is usually associated with accumulation of a group of dislocations round various obstructions (defects). The stress P_c sufficient to form cracks is expressed by Stroh's formula [23]:

$$P_c = \frac{12}{n} \cdot \frac{\sigma}{b},$$

where $\underline{n}$ is the number of delayed dislocations which depends on the porosity of the barrier; $\underline{b}$ is the magnitude of the Bürgers vector (interatomic distance in the glide plane). Consequently, as we usually assume, the strength of a substance falls with decreasing surface energy at the fresh surface of the crack, and rises on elimination of the accumulation of large avalanches of dislocations round the possible potential barriers.

In accordance with the well-known criterion of Ioffe, a substance is brittle when the yield point P_m is higher than the stress P_c required for rapid development of cracks, i. e., when

$$\sigma < \alpha b P_1,$$

* See footnote on page 1316.
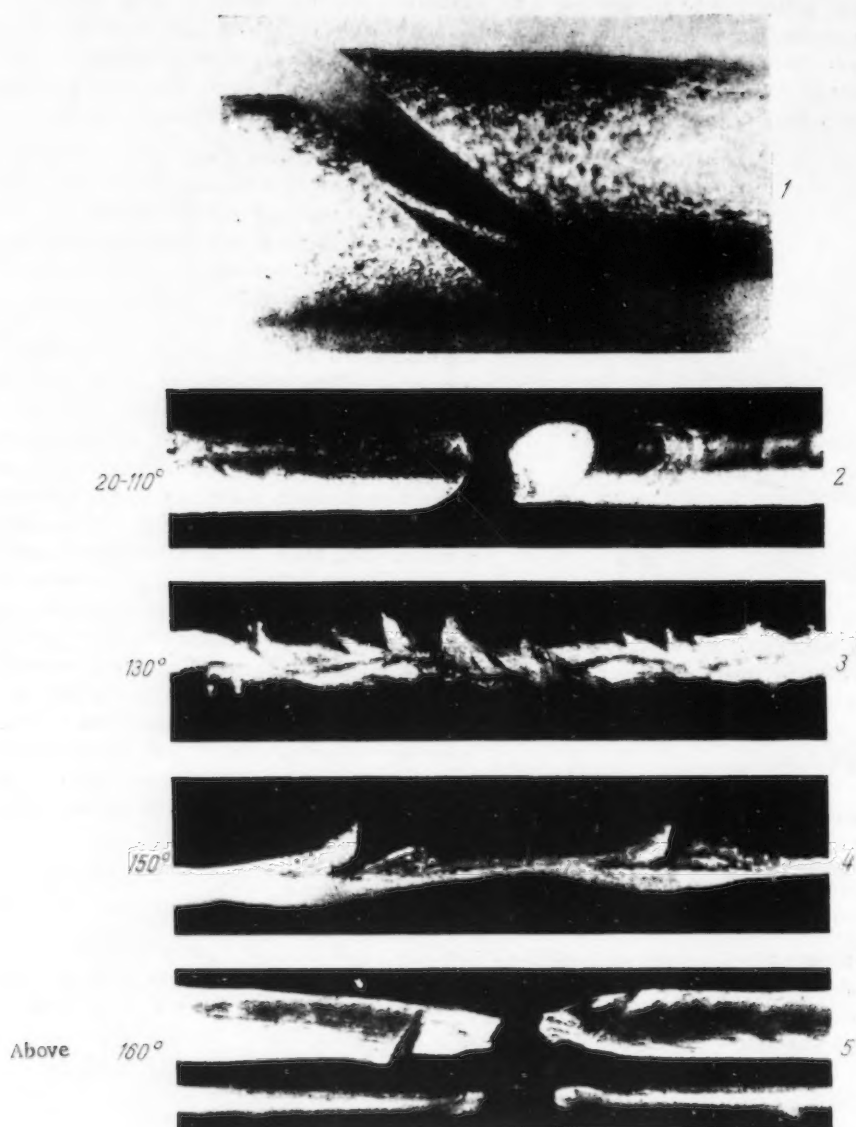
Fig. 6. Zinc monocrystals (diameter 0.5 mm, χ = 45°) (magnified 30 times), covered with a thin film of mercury (0.1μ), elongated at various temperatures: 1 and 2) brittle fracture with cleavage along the glide plane to 110°; 3) local brittle fractures over a background of plastic flow at t ≈ 130°; 4) the same, more strongly developed plastic flow; t ≈ 150°; 5) purely plastic rupture after elongation of ε = 200% (with elongation into a strip — photograph in two mutually perpendicular planes; t = 160° and higher.

where $P_1 = n \cdot P_m$ (the local stress necessary for overcoming the barrier , i. e., for propagation of the slip), α is a dimensionless constant (close to unity on the basis of theoretical considerations). This criterion corresponds to our criterion formulated above.

In accordance with the temperature dependence of the probability of development of a crack W, the probability of plastic flow, i. e., of overcoming the barrier by accumulation of dislocations $W_p = 1 - W$, is expressed by:

$$W_p = 1 - \exp\left(-\gamma e^{-\ln\frac{T_1}{T}}\right); \qquad \gamma = \frac{l}{b}\nu \cdot \tau_0 ,$$

Here ν is the proper frequency of the thermal vibrations of the atoms and is of the order of 10^{12}-10^{13} sec^{-1}; l is the length of the delayed front of the dislocations $l/b \approx 10^3$; τ_0 is the duration of accumulation of a group of dislocations sufficiently large for formation of a crack and is of the order of 10^{-3} sec; T_1 is the temperature at which there is a sharp rise in the probability of plastic flow from 0 to 1. This temperature

$$T_1 = \frac{1}{k \ln \gamma} \cdot U$$

is proportional to the energy of activation U for overcoming the barrier by the moving dislocations. Under our experimental conditions T_1 is approximately 150° and U is approximately 1 electron-volt/atom. As we see from Fig. 7, the relation between W_p and T is in good agreement with experimental data.
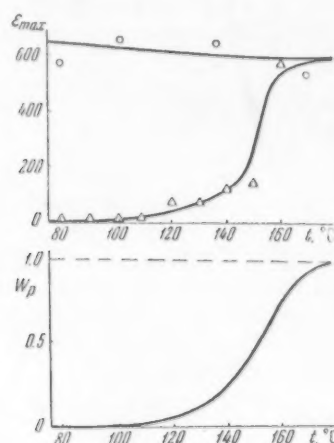

Fig. 7. Plasticity of the elongated (at $\frac{d\epsilon}{d\tau} = 15\%$

min^{-1} = const) zinc monocrystal, pure (circles) and covered with a thin film of mercury (triangles), as evaluated from the elongation at break $\epsilon_{max} =$

$= \left(\frac{l - l_0}{l_0}\right)_{max} \cdot 100\%$ as a function of the tempera-

ture. Transition from the brittle to the plastic state at higher temperature. Below is shown the theoretical curve for the probability of plastic flow W_p as a function of $\underline{t}$.

Adsorptive facilitation of deformation of metals under the action of surface-active greases plays a decisive part both in metal working (especially under pressure) and under the frictional conditions in the boundary lubrication of linked parts of machines. In processes of pressure fabrication (wire drawing or deep drawing in general) the grease ensures a high quality of the surface and a normal course of the process by considerably lowering the tractive force due to localization of the excess deformation of the metal in a thin, adsorptively softened film close to the surface [24].

On the other hand, the investigations in this field have enabled the strength of solids (especially metals) to be considerably increased by removal of the surface-active component in cases where frictional processes are absent, thus securing maximum firmness and load-bearing capacity of a given material in respect to static and periodic loads.

Elimination of low-melting, surface-active constituents from a metal or alloy is, as we see, an important condition for securing maximum strength at high temperatures, i. e., heat resistance; this is in full harmony with the investigations of Kishkin and co-workers [21]. It is interesting to note that these surface-active impurities are extensively used as modifying additives to ensure a finely crystalline structure during casting (adsorptive modification of crystallization) and are accordingly useful at ordinary (not high) working temperatures. As we now see, these useful additives can be extremely harmful at higher temperatures, especially under lengthy treatment.

Finally, as Lyubimova [25] showed in our laboratory, the adsorptive action of surface-active agents (greases) also permits a considerable increase in the rate of cold-hardening of a metal surface after increase of plastic deformation concentrated in thin films close to the surface. This type of hardening or enhancement of load-bearing capacity of a metal can also be secured by fatigue attrition in a surface-active medium below the fatigue limit, as was shown by Karpenko [16].

It is noteworthy that these effects are particularly conspicuous at temperatures intermediate between the regions of cold and hot working of a given metal, i. e., close to the temperature of commencement of recrystallization.

Some results of the work described in this report demonstrate the fruitfulness of collaboration between physical chemists, engineers, technologists, building engineers and metallurgists in the new field of physicochemical mechanics.

SUMMARY

1. Both of the main groups of problems of physicochemical mechanics are associated with problems of contemporary colloidal chemistry: 1) formation of three-dimensional disperse structures for production of hard substances (constructional and building materials with specific mechanical properties; 2) dispersion of solids — development in them of new surfaces in processes of deformation and breakdown during working under pressure, cutting and crushing.

2. Coagulated structures possess relatively low strength, complete thixotropy and very pronounced plasticity. Under low stresses their substantially unstressed structure undergoes slow flow with maximum viscosity which may exceed the minimum viscosity of a structure under maximum stress in flow by a factor of the eighth power. All the characteristics of coagulated structures are explained on the basis of the presence of thin residual layers of liquid medium at the sites of linking of the particles.

3. Coagulative structure-forming processes can be controlled by addition of agents that modify the shape, dimensions and linking conditions of the particles constituting the structure.

4. Crystallized structures formed by direct intergrowth of crystallites of a new phase, possess maximum strength, and are entirely free from thixotropy and plasticity. Plastic and elastic properties are imparted to such structures by the presence of elements of structure (crystallites or macromolecules), but these properties are lacking in the system as a whole. Development of crystallized structures constitutes the basis of processes of setting of mineral binders. For the purpose of obtaining dense, strong and durable concretes, the processes of structure-formation must be controlled by small admixtures of surface-active plasticizers and by mechanical vibration. This procedure slows down structure formation in the initial stage of preparation and placing in position of concrete mixes, and after completion of this period the structure formation is able to proceed with maximum speed.

5. Subsequent processes of recrystallization of intergrown portions, which are always thermodynamically unstable, lead to lowering of strength of the crystallized structures and can be the main cause of breakdown of concretes and other structural materials in the water-saturated state. These processes slow down and can substantially cease on transition to dense structures with a very small exposed porosity and with reduced solubility of the fresh hydrated forms.

6. Control of the processes of deformation and destruction of solids, metals for example, is possible by means of the adsorptive action not only of ordinary surface-active substances but also of melts or thin coatings of surface-active metals. These phenomena were studied by elongation of zinc monocrystals coated with thin films of tin or mercury, and are reflected in lowering of strength by a factor of ten and in embrittlement or (under small stresses) in a sharp rise in creep rate. Here the decisive factor is the temperature and the type of stress in association with the action of a surface-active agent or impurities.

7. The recorded observation enable control of processes of mechanical working of metals, structure formation, abrasion, and wear.

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NEW PROBLEMS IN THE FIELD OF CHAIN REACTIONS

N. M. Emanuel

(Report to the Session of the Division of Chemical Sciences of the Academy of Sciences of the USSR,

October 31, 1957)

Chain reactions are the basis of many processes in chemistry and physics and their discovery was a great achievement of science in the twentieth century.

Thanks to the researches of Academician Semenov and his school, credit for the discovery and development of the theory of branched chain reactions in chemistry must go to the Soviet Union. This theory, which has already been known for 40 years, provides an explanation, and enables prediction, of many facts and phenomena, ranging from striking examples of chain rupture with characteristic critical features to the mechanism of reactions with retarded development of chain avalanches (degenerate rupture). It must not be forgotten that the whole of the theory of chain branching reactions in chemistry has been factually recapitulated by physicists in the creation of a theory of the branched chain process of fission of nuclear fuel. It must be acknowledged that physicists have very much more extensively utilized the properties of chain branching reactions, and above all their capacity for autopropagation and autoaccelerative development. The diverse features of the chain branching mechanism can undoubtedly serve as a basis of development of new principles of controlled undertaking of chain reactions in chemistry.

Recently we have succeeded in drawing attention to a series of complications of the classical picture of development of chain reactions for multicomponent systems. The phenomena thereby revealed enable us to put forward some new concepts concerning the efficient control of the process of chemical transformation. The investigations in question related to slowly proceeding nonstationary reactions of oxidation of hydrocarbons and other organic compounds. It is evident that the study of these reactions is not only of theoretical but also of great practical interest. The present report is devoted to new problems in the field of slow chain branching reactions.

Initiation of Slow Chain Reactions of Oxidation of Hydrocarbons in the Liquid Phase

The slow growth of a chain avalanche in the oxidation of hydrocarbons is due to the rarity with which chain branching occurs; the branchings occurs; .the branchings appear to be "too late" with respect to the time of development of the main chain of the oxidation reaction. Autoacceleration is consequently a long drawn-out process.

The kinetic law of the initial autoacceleration of a slow chain-branching reaction depends essentially on the type of rupture of the chain that is dominant. If the chain is ruptured by homogeneous recombination of free radicals, then the over-all number of products of oxidation P in the initial period of development of the process grows with time in proportion to t^2. But in the case of linear rupture of the chain, the value of P in a chain with a degenerately branched type of reaction increases proportionally to $e^{\varphi t}$. The latter relation distinctly applied to hydrocarbon oxidation processes in the gas phase. The kinetic curves of liquid-phase oxidation, however, likewise in part (in the initial portions) satisfactorily approximate to the exponential law. Characteristic of oxidation reactions of liquid hydrocarbons are more or less long induction periods which in some cases can extend to many tens and even hundreds of hours. From the standpoint, therefore, of the chemical researcher and of the technologist interested in the manufacture of oxidation products, the induction period is a useless waste of time, and the elimination of this period is part of the problem of controlling the oxidation process.

The magnitude of the induction period depends upon the rate of production of chains. In the initial period of development of the process, when there is still little of the branched chain of the intermediate product, the only reaction supplying free radicals is the elementary act of production of chains. It is usual to stimulate the slow, chain-branching reactions by addition of substances capable of forming free radicals or of breaking down to free radicals or of forming them by reaction with components of the reacting mixture. Thus, the process of hydrocarbon oxidation can be promoted by additions of peroxides, aldehydes, ketones, and by introduction into the reaction zone of catalysts such as salts of metals of varying valence. The problem can be formulated more widely by turning our attention to the fact that the promotion of slow chain-branching reactions can be realized not throughout the course of the whole reaction but only in the initial period of its development. By "triggering" a chain-branching process, it can be made to proceed with increased velocity at the expense of branchings of the chain. The theory of the initial "impulse" can be illustrated by means of the simplest chain reaction scheme in which degenerate branchings occur due to transformations of the substance which is the end product of the reaction. In this case the system of kinetic equations on the assumption of linear rupture of the chain can be written as follows:

$$\frac{d(R)}{dt} = w_0 + k_1(X) - k_2(R);$$
$$\frac{d(X)}{dt} = k_3(R),$$

where w_0 is the rate of formation of the initial active centers; R is the radical bearing the chain; X is the final product of oxidation (also the branching agent); $k_1(X)$ is the velocity of degenerate branching; $k_2(R)$ is the velocity of chain rupture; $k_3(R)$ is the velocity of oxidation (formation of product X).
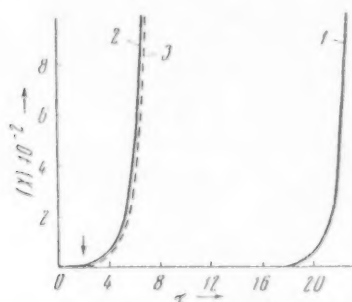

Fig. 1. Initiation of chain reactions with degenerate branchings by increasing the velocity of generation of the initial active centers (radicals): 1) kinetic curve of the noninitiated reaction $(X) = 10^{-7} \cdot (e^T - 1)$; 2) initiated reaction under the continuous action of the initiator $(X) = (e^T - 1)$; 3) development of process under the action of an initiator in the initial period up to $\tau_1 = 2.3$ and stoppage of supply of initiator after the instant of time $(X) = 0.9\,e^T$.

Assuming constancy of concentration of free radicals and introducing the relevant terms:

$\tau = \frac{k_3 k_1 t}{k_2}$ (relative time) and $\omega_0 = \frac{w_0}{k_1}$ (relative rate of development of active centers), we obtain:

$$\frac{d(X)}{d\tau} = \omega_0 + (X),$$

On integrating this differential equation we obtain the expression:

$$(X) = \omega_0(e^\tau - 1) \approx \omega_0 e^\tau.$$

Oxidation will follow this law of self-acceleration in the case of "natural" growth of chains with a velocity of ω_0. In the case of artificial creation of active centers in a system and their continuous generation with a velocity greater than ω_0, for example, with a velocity ω_{0k}, the following analogous expression for X can be written:

$$(X) = \omega_{0k}(e^\tau - 1) \approx \omega_{0k} e^\tau.$$

Kinetic curves corresponding to the two last expressions are plotted in Fig. 1 on the assumption that $\omega_0 = 10^{-7}$ and $\omega_{0k} = 1$. In other words we assume that the catalyst (initiator) exceeds by 10^7 the velocity of production of chains. The shortening of the induction period of the reaction is striking.

If the artificial generation of active centers with increased velocity is realized only in the course of a short period of time τ_1, at the start of the process, and is then stopped and only the "natural" generation with velocity ω_0 remains in play, we find for X:

$$(X) = [\omega_{0k} - (\omega_{0k} - \omega_0)\,e^{-\tau_1}]\,c^\tau - \omega_0.$$

With sufficiently large values of τ_1, the factor $e^{-\tau_1}$ quickly becomes so small that the magnitude of $(\omega_{0k} - \omega_0)\,e^{-\tau_1}$ can be neglected in comparison with ω_{0k} and hence:

$$(X) = \omega_{0k}e^\tau - \omega_0.$$

Finally, after the lapse of a short period from the start of the reaction, $\omega_{0k}\,e^\tau$ becomes very much greater than ω_0, and we obtain:

$$(X) \approx \omega_{0k}e^\tau,$$

identical with the formula for X in the case of continuous generation of chains with a velocity of ω_{0k}. The kinetic curve of the reaction with short-period stimulation of it over a period τ_1 is also plotted in Fig. 1 (dashed curve).

It is easy to see that short-period initial stimulation is sufficient for appreciable shortening of the induction period. For a closer analysis of the problem we must take into consideration the ratio between the velocity of generation of chains and the velocity of degenerate branching at the instant of stoppage of the artificial stimulus. If at this instant the velocity of formation of chains is already appreciably smaller than the velocity of degenerate branchings, the stoppage of the stimulus should be usbstantially unobservable. But if both of these magnitudes did not differ appreciably, a more or less sharp discontinuity should have been registered on the kinetic curves at the instant of stoppage of the artificial stimulus.

By what methods could the initial stimulation of slow chain-branching reactions of oxidation in the liquid phase be realized ? In the last 2-3 years we have suggested several such methods which are relatively simple and presumably realizable. These are gaseous initiation; the initial triggering action of the γ-radiation of Co^{60} and of the radiation of radioactive inert gases under conditions possibly permitting development of a chain reaction; short-period action of salt catalysts (initiators). In all cases the effect of short-period triggering actions can to a first approximation resolve itself into an artificial increase of the velocity of formation of active centers in the initial period of development of a chain reaction with degenerate branching.

Gaseous initiation. The method of gaseous initiation consists essentially in the passing through the mixture, in addition to air or oxygen, a small quantity of a gaseous catalyst (initiator) assumed to be capable of increasing the rate of chain formation. When the initiating gas has been passed through for a short period, the feed can be easily cut off and the oxidation by air or oxygen alone should proceed with increased velocity due to the accumulation in the system of a sufficient quantity of the branched chain of the intermediate product.

We proposed and tested the following as gaseous initiators: NO_2, a substance of a radical character due to the presence in its molecule of an odd number of electrons; O_3, which contains an excess of oxygen atoms functioning as bivalent radicals; Cl_2, HBr, etc. Short-period action of small quantities (sometimes fractions of a percent) of these gases on the oxidation process led to striking effects of initial stimulation in many cases (liquid-phase oxidation of n-decane, n-hexadecane, isodecane, n-butane and paraffin wax). Short-period initiation is less effective than continuous stimulation in the case of oxidation of cyclohexane, benzene and diphenylethane. This signifies that in the instant of stoppage of the initiation the rate of reaction of the degenerate branches is of the same order of magnitude as that of the formation of chains.

Special attention is merited by the application of the principle of short-period gaseous initiation for the purpose of promotion of the oxidation of liquefied hydrocarbon gases. We selected n-butane as the material for an investigation in this field. The critical temperature of n-butane is 153° and its critical pressure is 36 atmos. By employing a relatively low pressure there is consequently a definite possibility of carrying out the oxidation of n-butane not in the gas phase (as is usually the case) but in the liquid phase. It is natural that the processes of far-reaching oxidation which make the results of gas-phase oxidation so disappointing will not be developed to any great extent due to the low operating temperature. At 145°, for example, the noninitiated oxidation of n-butane develops extremely slowly since there is a long induction period. In presence, however, of NO_2 (addition of NO_2 to an equimolar mixture of nitrogen and oxygen in the proportion of about 0.5% by volume) only a 10-15-min initiation period suffices for commencement of a rapid oxidation of n-butane to acetic acid and methyl ethyl ketone (Fig. 2). After 12-14 hrs about 50% of the butane is oxidized with a high degree of selectivity
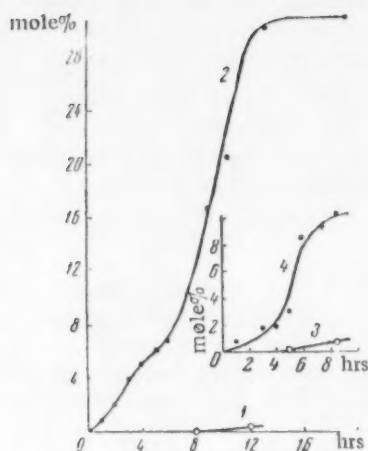
Fig. 2. Kinetic curves of formation of acetic acid by oxidation of n-butane in the liquid phase: 1 and 3) non-initiated reaction to acetic acid and methyl ethyl ketone; 2, 4) after short-period promotion of the reaction with NO_2 to given acid and ketone, respectively.

to form two valuable products — acetic acid ($\sim$ 30-50%) and methyl ethyl ketone ($\sim$ 10-12%). The characteristics of the initiating action of NO_2 on the oxidation of n-butane in the liquid phase are now being closely investigated by the author in collaboration with Blyumberg and Maizus.

The author and Voronkov have very recently observed the oxidation of n-butane to acetic acid using ozone as initiator even at the low temperature of 85° (pressure in the system $\sim$ 10 atmos, ozone passed through continuously in the proportion of 0.25 vol.% of the amount of oxygen used for the oxidation).

There are many other processes in which far-reaching destructive oxidation, characteristic of high-temperature reactions in the gas phase, is the main obstacle to the production of valuable oxygen-containing products by direct oxidation. Such processes undoubtedly include the oxidation of benzene to phenol. In collaboration with Denisov the author recently demonstrated the fundamental possibility of liquid-phase oxidation of benzene to phenol at temperatures close to the critical temperature by employing gaseous initiation with NO_2. As already mentioned continuous gaseous initiation is more effective in this case. Continuous gaseous initiation with NO_2 was likewise found by the author and Denisov to be extremely effective for the promotion of the oxidation of cyclohexane to adipic acid in the liquid phase under pressure.

These results permit us to consider the question of the expediency of converting a number of processes of high-temperature gas-phase oxidation to regimes of low-temperature liquid-phase oxidation with gaseous initiation. In a number of cases the short-period action of gaseous initiators has proven effective.

Likewise noteworthy are the interesting long-term investigations of the kinetic differences between liquid-phase and gas-phase reactions. Such investigations may involve study of reactions in one and the same chemical system (for example, butane—air) with passage from the liquid phase through the critical point into the vapor phase at high densities and finally into the normal gas-phase system. Consequently the study of processes of oxidation of liquefied hydrocarbon gases at temperatures close to the critical temperature is in itself a problem of great theoretical and practical interest which takes us far outside the framework of the example that we employed to illustrate the concept of the starting "point" of a branched-chain process.

Work by the author and Blyumberg has revealed the striking effect of short-period gaseous initiation with the help of NO_2 in the process of oxidation of paraffin wax to synthetic fatty acids; in collaboration with Voronkov the same authors have also demonstrated the possibility of a considerable reduction in the temperature of oxidation of paraffin wax when using ozone as gaseous initiator. The author, Berezin and Vagner have demonstrated the possibility of short-period triggering of the oxidation of paraffin wax by small additions of chlorine to the oxidation air.

Many authors in different laboratories of the Soviet Union are now employing gaseous initiation of liquid-phase chain reactions of various substances. Consideration is being given in this connection not only to slow, nonstationary processes but also to chain reactions with unbranched chains such as, for example, chlorination reactions (Topchiev, Krentsel, Kornev, and others).

Triggering action of the γ-radiation of Co^{60} in the initial period of development of a slow, nonstationary process. The above discussion is interesting in connection with the problem of utilizing the action of a penetrating radiation for improving the efficiency of chemical reactions. It is natural that the action of penetrating (ionizing) radiations, which resolves itself into the release of free atoms and radicals, should be useful for initiation of chain reactions. The first systematic investigations of the action of radiation (x-radiation, electron stream)

on processes of oxidation of various organic compounds with molecular oxygen were carried out by Bakh and co-workers. In these investigations, notwithstanding the high doses of radiation, oxidation products were detected in small quantities. A distinguishing feature of the experimental conditions was the relatively low temperature (0-60°) and the continuous irradiation of the chemical system throughout the entire reaction.

The action of penetrating radiation on the process of oxidation was therefore studied under such conditions that no long chains could develop due to the low temperature. The low yield of oxygen-containing products was therefore mainly due to the relatively small number of radical reactions resulting from the direct action of the radiation without development of chains. In all probability the low yield of products was also associated with the continuous nature of the radiation effect which caused the products of oxidation to be involved in further radio-chemical processes side by side with the original hydrocarbon.

We effected oxidation by a high-temperature process with the objective of exploiting the effect of penetrating radiation as a means of increasing the initial rate of formation of chains under such conditions that the chain reaction could be self-sustaining with development of sufficiently long chains. In addition, bearing in mind the chain-branching mechanism of the oxidation process, irradiation was effected not throughout the whole period of reaction but only in the initial period of its development. By this means we hoped to protect the oxidation products against subsequent radiolysis.
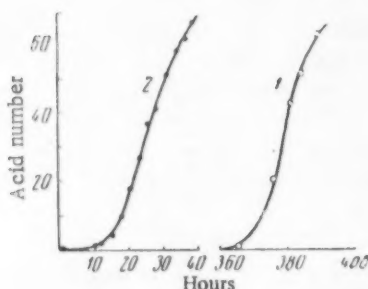

Fig. 3. Promotion of the chain reaction of oxidation of paraffin wax with the help of the γ-radiation of Co^{60} in the initial period of the process: 1) nonpromoted reaction; 2) progress of process after short period exposure to a small dose of γ-radiation.

The process selected for investigation was the oxidation of "Kepsen" grade of paraffin wax (GDR). In the absence of a catalyst this paraffin is oxidized extremely slowly at 127°, and the induction period is of the order of 370 hrs, presumably due to the presence of oxidation-inhibiting impurities. The picture changes when the paraffin wax undergoing oxidation at this temperature is subjected to short-period (70 min) exposure to the γ-radiation of Co^{60} in a dose of the order of 100 r. This treatment is sufficient to cut down the induction period on further oxidation (without further irradiation) from 370 to 12 hrs (Fig. 3). The results confirm our theory of the efficient utilization of the action of penetrating radiations, and bear witness to the necessity for detailed investigations of the action of penetrating radiations under conditions permitting the development of a slowly growing, self-sustaining chain reaction.

As we known, Proskurin and co-workers recently also established the occurrence of an initial promoting effect of the γ-radiation of Co^{60} on the oxidation of cetane (n-hexadecane). The rate of formation of acids in the oxidation of cetane at 130° after short-period (about 30 min) exposure to γ-radiation considerably exceeds the reaction rate in the absence of radiation. More prolonged irradiation does not lead to further rise of reaction rate.

In work with Dzantiev and Pomansky, the author has now obtained preliminary results of the promotion of oxidation of paraffin wax when an ampoule of paraffin wax containing dissolved oxygen was subjected to irradiation in the active zone of a nuclear reactor. There is no doubt that the radiation from a nuclear reactor must be applied for short periods, i.e., the mixture of chemical reactants must have only a short residence time in the active zone.

These conditions were not fulfilled in the experiments in question. The ampoule remained in the reactor for about 3 hrs where it was exposed to the action of a powerful neutron stream ($\sim 10^{13}$ neutrons/cm$^2 \cdot$ sec) and intense x-radiation ($25 \cdot 10^6$ r/hr). In subsequent oxidation of the paraffin wax which had undergone the above treatment, the induction period was reduced from 370 to 10-15 hrs. In other words, substantially the same result was obtained as in the experiments with small doses of radiation, although the experimental procedure was not the same in both cases.

We consider the further study of the promoting effects of penetrating radiations in the active zone of a nuclear reactor to be of potential value when employing short residence times followed by reaction outside the reactor but under conditions permitting development of a self-accelerating chain reaction.

Initiation of chain reactions by the action of the radiation of radioactive inert gases. The idea of utilizing radioactive inert gas radiations for initiation of chain reactions occured to us as a logical sequel to the principle of gaseous initiation with chemically active gases and of the promoting effect of penetrating radiations. At the present time the experimenter can use Xe^{133}, Kr^{85} and Ar^{41} in addition to the radioactive emanations (radon, thoron and actinon). All of the three radioactive isotopes can be obtained from the respective inert inactive gases by the (n, γ) reaction. Xe^{133} and Kr^{85} are also products of fission of U^{235} and Pu^{239} and are isolated in the purification of blocks of nuclear fuel slagged up by fission products. Employment of inert radioactive gases permits all of the three types of radiation (α, β and γ) to be used for initiation purposes at various energy values. In addition, the α- and β-particles emitted from the radioactive atoms directly enter the reaction system and exert their action uniformly through the entire mass of liquid. This is very important since the introduction of these particles into the reaction vessel from an external source is associated with enormous difficulties or is altogether impossible due to their intense absorption by the wall of the vessel or the material of the inspection window.
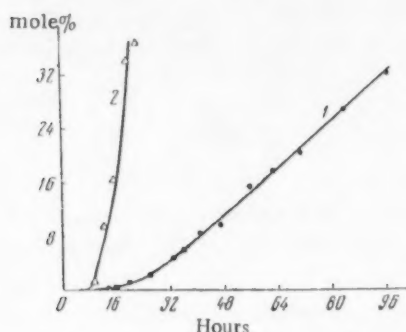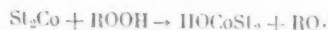

Fig. 4. Effect of initial promoting action of Rn^{222} radiation in the process of oxidation of isodecane (2,7-dimethyloctane): 1) formation of acids in the unpromoted reaction; 2) development of process of enrichment with acids due to initiation of the reaction with the α-radiation of radon.

It seems to us that radiations from radioactive gases must be an efficient means of initiation not only of slow branched chain reactions but also of unbranched liquid-phase chain reactions. There is also no doubt that radioactive inert gases enable interesting experiments with gas-phase chain reactions to be undertaken.

In the present report we shall illustrate the possibilities of using the radiation from radioactive inert gases by the example of the initial promotion of the oxidation of isodecane (2,7-dimethyloctane) with the α-particles of radon Rn^{222}. Experiments were instituted by the author with Blyumberg, Ziv and Pikaeva. The choice of Rn^{222} as initiator cannot be considered an altogether happy one since its breakdown yields several secondary radioactive products. However, the promoting effect of a minute quantity of Rn^{222} (a total of $7.2 \cdot 10^{-6}$ cc), introduced together with 1.5 liters of oxygen over a period of 60 min, was so intense that we can certainly speak of a process of initial promotion (Fig. 4).

The effect of the above-mentioned quantity of Rn^{222} is equivalent to the general dose of emission ~ 500 r. Thus, in this case, we witness the strong action of small doses of irradiation which cause the development of a chain reaction of chemical conversions.

Characteristic effects of salt catalysts (initiators). One of the most widely used methods of initiation of processes of oxidation of hydrocarbons and other organic compounds in the liquid phase is that employing salts of metals of variable valence. If a system already contains peroxides, the mechanism of the initiating action of salt catalysts, e. g., stearates of bi- and trivalent Co, consists in the formation of free radicals according to the reactions:

$$St_2Co + ROOH \rightarrow HOCoSt_2 + RO \cdot$$

$$St_3Co + ROOH \rightarrow St_2Co + RO_2 \cdot + HSt.$$

If the system only contains a hydrocarbon at the start, then chain-formation reactions are hypothetically possible:

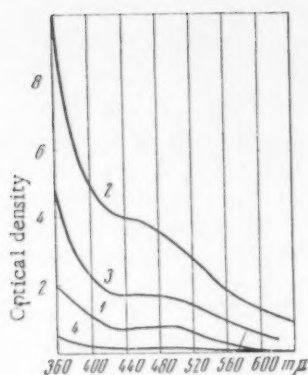$$St_2Co \cdot O_2 + RH \rightarrow St_2Co - OOH + R \cdot$$

Fig. 5. Absorption spectra of the reacting system in the oxidation of n-decane at 140° in presence of 0.3 mole% of manganese laurate (1 — after 5 min; 2 — after 12 min; 3 — after 20 min; 4 — 30 min after start of experiment).
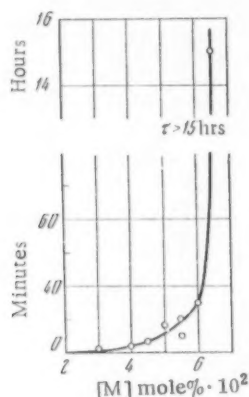

Fig. 6. Kinetics of accumulation of carbonyl compounds in the oxidation of n-decane at 140°; 1) without catalyst; 2) with 0.3 mole% Co$(C_{17}H_{35}COO)_2$; o) the same with removal of catalyst by precipitation (duration of removal in different experiments shown by arrows).

Fig. 7. Phenomenon of the critical concentration of copper stearate in the catalytic oxidation of n-decane. Induction period as a function of catalyst concentration at 140°.

or

$$St_2Co \cdot O_2 + RH \rightarrow St_2Co - OH + RO \cdot$$

According to these equations cobalt stearate initially forms a molecular complex $St_2Co \cdot O_2$ with oxygen.

It is extremely probable that such elementary processes do indeed occur in the reacting system. In the past 20-30 years, however, many investigators have reported that in the initial period of the process there is a rapid change in the valence state of the metal, at first predominantly in the direction of formation of a form of higher valence followed mainly by transition to the form of lower valence. Tsyskovsky and co-workers showed the occurrence of this phenomenon with especial clarity in the case of catalysis of the oxidation of kerosene fractions of petroleum with manganese naphthenate. It was shown that the cycle of valence transformations of the catalyst is concluded by its precipitation. At the same time the oxidation reaction continues according to a regime characteristic of a catalyzed reaction. Numerous instances of initial microscopic transformations of salt catalysts were subsequently observed by foreign workers as well as by Zeinalov, the present author and his co-workers. As an example we may mention the change in absorption spectrum of the reacting mixture during the oxidation of n-decane in presence of 0.3 mole% of Mn$(C_{11}H_{23}COO)_2$ (Fig. 5). The whole cycle of valence transformations of manganese laurate occupies 40 min during an oxidation period of about 10 hrs.

Since this cycle is quickly completed, it is pertinent to inquire what part is played by the precipitate of catalyst in the further course of the oxidation. With this objective, the author with Vartanyan, Knorre and Maizus studied the kinetics of oxidation of n-decane after removal of the precipitate of catalyst. The experiment showed that the kinetic curves of formation of alcohols, carbonyl compounds, acids and esters remain the same as in oxidation in presence of the precipitated catalyst. Only peroxy-compounds behave differently — their concentration starts to increase rapidly after removal of the precipitate, and the kinetics of their accumulation resembles that in noncatalyzed oxidation. Here the presence of the precipitate speeds up the process of breakdown of peroxides. This is illustrated by Fig. 6 in which the kinetic curve of growth of quantity of carbonyl compounds in experiments in the presence of catalyst and after removal of the precipitated catalyst is plotted. In the theoretical treatment of
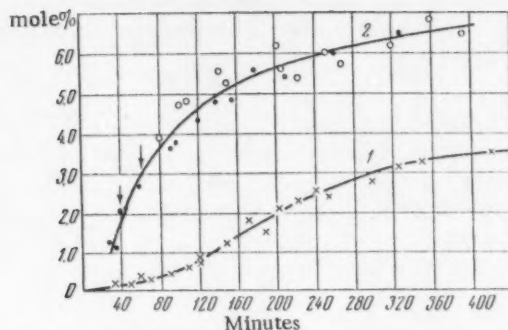
these data, we must assume that the initial cycle of transformations of the catalyst is accompanied by formation of a metal-free intermediate substance (or a number of products) which brings about an increased velocity of the reaction after removal of the catalyst precipitate. This would explain why the kinetic curves of formation of the main products of oxidation "do not reflect" the period of rise of concentration of peroxy-compounds from the steady value characteristic of a catalyzed reaction to a steady value corresponding to a noncatalyzed regime. From the standpoint of the general concept developed in this section of the report, the experiments on removal of the precipitated catalyst can be interpreted as cessation of the action of the initial impulse triggered off by the salt catalyst.

Recent work by the author, Knorre and Chuchukina has clearly shown that the behavior of a catalyst in the system containing the hydrocarbon feedstock is generally even more complicated since the catalyst functions not only as an initiator but also as an oxidation chain breaker. Rise of concentration of the catalyst is accordingly accompanied by an induction period while the faster reaction following emergence from a previous induction period is maintained. These two functions result in the manifestation of a critical phemomenon which takes the form of a sharp increase in the induction period when the catalyst concentration reaches a critical value (Fig. 7). This phenomenon may serve as one of the strongest proofs of the chain-branching mechanism of liquid-phase hydrocarbon oxidation reactions.

The foregoing facts point to the existence of a regulating function of salt catalysts, i. e., to their ability to maintain a definite ratio between the products of oxidation; in this connection it becomes clear that the study of the mechanism of salt catalysis is now (as formerly) of very great importance in the liquid-phase oxidation of organic substances.

Macroscopic Stages and the Mechanism of the Action of Homogeneous Catalysts and Inhibitors in Chain Reactions

In many cases a detailed analysis of the chemistry of oxidation processes from the kinetic aspect clearly reveals their macroscopic gradation. The occurrence of diverse parallel, consecutive and conjugated macroscopic stages in oxidation reactions has been known for a long time. What is new is our observation of the widespread occurrence of changes of regime of reactions during their course, i. e., transitions from one macroscopic stage to another after a short interval of time. In the case of simple consecutive reactions there is continuous formation of intermediate substances and their conversion to the final products throughout the entire course of the process. In the case, however, of a sequence of macroscopic stages separated in time, the first process is completed without the original substances being used up and gives way to the second stage. The duration of the second stage depends upon how far-reaching the first one was, and the over-all reaction may likewise come to an end without the original substances being used up. In individual cases the impression is created that we are dealing with an initial self-inhibiting reaction which takes place during the induction period of some main process. Here the conjunction of the two processes has the distinguishing characteristic that the second macroscopic stage consumes the products formed during the first stage, i. e., the end products of the first stage are, as it were, some of the starting products of the second stage. Ultimately, in relation to the over-all process of oxidation, the kinetics of change of concentration of the products of the first stage are outwardly identical with the kinetics of the intermediate products of the subsequent reactions.

Our first observations of such a change-over of oxidation regimes (in collaboration with Maizus) were in connection with the gas-phase oxidation of acetaldehyde. The first stage in oxidation with oxygen is formation of acetyl hydroperoxide and acetic acid. When about half of the original amount of acetaldehyde has been consumed, there is an abrupt stoppage of the oxidation by oxygen (the O_2 concentration remains unchanged from this instant up to the end of the process) and an acetyl hydroperoxide — acetaldehyde interaction commences without participation of oxygen. The end products of this second stage are acetic acid and gases (CO, CO_2, C_2H_6 and H_2O). The pressure conditions change at the same time; instead of falling, the pressure rises (Fig. 8). The second macroscopic stage (oxidation with peroxide) thus confirms, from a fresh aspect, the validity of the classical peroxide theory of Bakh.

A similar picture was recently observed by the author with Babaeva and Maizus in a study of the oxidation of isobutane in presence of HBr in the gas phase. Here there is likewise observed stoppage of the process of oxidation of isobutane by oxygen, with formation of tertiary butyl hydroperoxide, and transition to the second change (oxidation of isobutane by the hydroperoxide formed in the first stage) (see Figs. 9 and 10). Substantially the sole
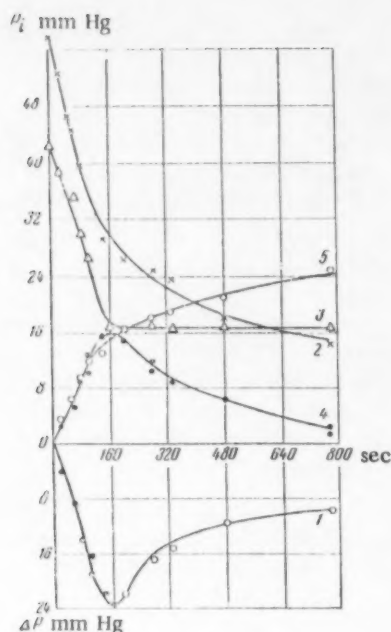
Fig. 8. Distribution of components in the reacting mixture of acetaldehyde and oxygen at 170° and at a total initial pressure of the mixture of $CH_3CHO + 0.75 O_2$ of 100 mm Hg. Change of pressure during the reaction (curve 1). Change of concentration of acetaldehyde (curve 2), of oxygen (3), of acetyl hydroperoxide (4), and of acetic acid (5).

Fig. 9. Distribution of components in the reacting mixture of isobutane and oxygen in presence of HBr at 170°. Composition of starting mixture 125 mm i-C_4H_9 + 63 mm O_2 and 12 mm HBr. Change of concentrations: 1) of isobutane; 2) of oxygen; 3, 4) rise in content of gases (CO and CO_2).

product of the first stage is tertiary butyl hydroperoxide (apart from a small quantity of tertiary butyl alcohol).

It is quite evident that from the moment of development of the second stage, acetone and gases (CO, CO_2, H_2O) appear in the system, and the process of accumulation of the alcohol continues. The occurrence of a sequence of macroscopic stages separated in time can be most conclusively demonstrated by the study of the heat released by the reacting mixture in the course of the reaction. In complex systems, when gaseous hydrocarbons are oxidized in presence of homogeneous positive catalysts, two regimes of heat development, separated in time, are clearly observed; these reflect the two macroscopic stages which are staggered in time. Investigations along these lines were carried out by the author in collaboration with Maizus (oxidation of propane in presence of HBr, NOCl and NO_2), with Sedova (oxidation of ethane in presence of HBr), with Kruglyakova (oxidation of propane in presence of Cl_2); their results are plotted in Fig. 11.

Fig. 10. Distribution of components in a reacting mixture of isobutane and oxygen under the conditions of Fig. 9. Change of concentrations: tertiary butyl hydroperoxide (1); tertiary butyl alcohol (2); acetone (3).

The oxidation of propane in presence of HBr was studied in the greatest detail. This reaction leads to nearly selective oxidation of propane to acetone which is formed (under specific conditions) in accordance with the extremely simple kinetic law:
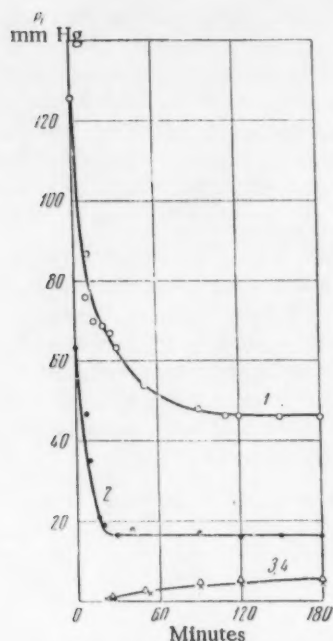
Fig. 11. Photorecording of the heat developed by reacting mixtures which point to the existence of two regimes of heat liberation (two macroscopic stages in the mechanism of homogeneous catalysis of processes of hydrocarbon oxidation): 1) oxidation of propane at 200° (catalyst HBr); 2) oxidation of ethane at 266° (HBr); 3) oxidation of propane at a) 319°, b) 324°, c) 333° (NO$_2$); 4) oxidation of propane at 285° (NOCl); 5) oxidation of propane at 327° (Cl$_2$). Time recordings (vertical lines) are given at intervals of 30 sec.

$$(CH_3COCH_3) = (CH_3COCH_3)_\infty (1 - e^{-kt}).$$

The applicability of a simple kinetic law of the first order for formation of a product in a complex three-component system was unexpected. On the basis, however, of the concept of macroscopic stages, the whole of the experimental data for this reaction can be interpreted.

The first stage (distinctly recorded on the heating curves) leads to an intermediate product I, for example, one of the oxyacids of bromine (HBrO, HBrO$_2$). At the end of the first stage the concentration of intermediate product is I_0. Shortly before the end of this stage the oxidation of propane to acetone sets in quite intensively due to breakdown of the intermediate product I. If each act of monomolecular breakdown of product I (say into OH and Br radicals) initiates a chain of oxidation of propane to acetone with a mean length of ν, then the reaction terminates with formation in system of $I_0\nu$ molecules of acetone. The kinetic law of formation of acetone will have the form

$$(CH_3COCH_3) = I_0\nu(1 - e^{-kt}),$$

i. e.,

$$(CH_3COCH_3)_\infty = I_0\nu.$$

The reaction terminates long before consumption of the starting substances; its extent depends upon the intensity of the first initiating macroscopic stage which is, presumably, a branched-chain, self-inhibiting reaction.

In all cases of development of a two-stage process (see Fig. 11), this is associated with the introduction of a catalyst. The mechanism of the catalyzing (initiating) action of many homogeneous additives must accordingly be considered as the result of an initiating macroscopic stage in the initial period of development of the over-all reaction. Subsequently, the products of the initiating reaction induce the later macroscopic stages by one mechanism or another. In this connection, in a number of cases the scale of the second stage or of the over-all process is governed to a large extent by the intensity of the initiating reaction. This is a new point of view of the mechanism of the initiating action of homogeneous additives (initiators and catalysts) in slow chain-branching processes. In the same connection it is interesting to note also new features of the action of negative catalysts (inhibitors) associated with the stagewise mechanism of oxidation processes.

If the consecutive macroscopic stages that we have just considered are chain reactions with a large number of diverse elementary steps, then the action of inhibitors at the different stages must in principle be different. In other words, compounds which are inhibitors for the first macroscopic stage cannot exert any action on the second stage, and conversely. There are possibilities of suppression of an over-all process due to destruction by an inhibitor of the product formed in the initiating stage, and so forth. Consequently, we have a new approach to the problem of the mechanism of inhibitor action in complex chain processes which involves some macroscopic stages.

As an example of the suppression of an over-all process by the action of additives at the initiating macroscopic stage we may cite the drop in final yields of acetone in the oxidation of propane in presence of HBr when acetone is added to the starting mixture. The
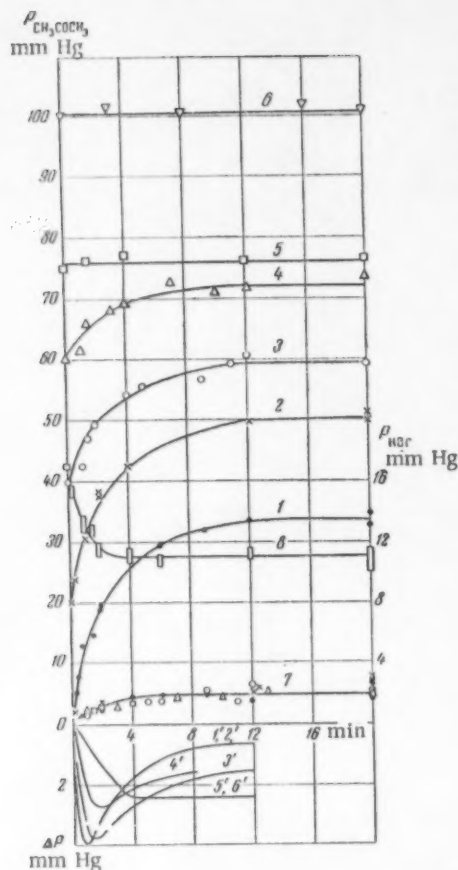

Fig. 12. Suppression of the process of formation of acetone by additions of acetone to a starting mixture of propane and HBr: 1) kinetic curve of formation of acetone in a mixture of 80 ml propane + 80 mm oxygen + 17 mm HBr; 2) the same with addition to the starting mixture of 20 mm acetone; 3) the same with addition of 40 mm acetone; 4) the same with addition of 60 mm acetone to starting mixture; 5) the same with addition of 75 mm acetone (limiting concentration); 6) the same with addition of 100 mm acetone (above the limiting concentration); 7) kinetic curve of formation of acids under conditions 1-6; 8) kinetics of the consumption of HBr for conditions 1-6; 1'-6' kinetic curves of reaction plotted for changes of pressure under cond. 1-6.

inhibiting effect of acetone is only manifested if the additions are made to the starting mixture or during the development of the first initiating stage. The later the additive is added the smaller is its effect. Finally, on introducing even large quantities of acetone after completion of the initiating stage, no changes at all in the acetone yield are observed. This signifies that acetone inhibits only the initiating macroscopic stage and has no action at all on the second stage induced by the products of the first stage.

The fall in acetone yield (when the kinetic law is obeyed) is plotted in Fig. 12 as a function of the amount of acetone added to the starting mixture. If the maximum concentration of additive (75 mm Hg) capable of completely suppressing the formation of acetone is added 15-20 sec after the start of the reaction, no inhibiting action is observed.

It is easy to visualize the great possibilities of investigation of the action of inhibitors introduced into a reacting mixture at different stages of development of a process.

In conclusion it should be noted that the features of the action of salt catalysts in the oxidation of hydrocarbons in the liquid phase, discussed above at length, are also proof of the existence of macroscopic, consecutive stages.

The Problem of the Control of Chemical Chain Reactions in Connection with the Existence of Macroscopic Stages

The existence of macroscopic stages directly leads on to the concept of the development of new methods of influencing a true complex process by means of various chemical and physical agents at different macroscopic stages. The deliberate aim of carrying out many complex reactions under conditions strictly laid down from the start (pressure, temperature, composition of mixture, catalysts, inhibitors, etc.)must be considered incorrect. Similarly, a timely and active intervention in the course of a process has not been envisaged. Moreover, different macroscopic stages will be differently related to the specified conditions. It is not at all inevitable that conditions favorable for realization of initiating stages will be also optimum for consecutive stages induced by the initial stage. This signifies that the efficient conduct of a complex reaction necessitates alteration of the operating conditions in the course of the reaction (change of temperature and composition of mixture, introduction and removal of catalysts, creation of artificial initiating stages of the type of gaseous initiation, and so forth).

The slow development of a chain avalanche in the oxidation of hydrocarbons makes this class of processes extremely suitable for the application of a variety of effects of practical value for the reaction course. Macroscopic stages and the products of these stages (intermediate and end products of a molecular character) are more accessible to study than the elementary processes, and they should therefore be mainly considered in connection with the control of a complex process.

At the present stage of development, the chain theory has already progressed beyond the study of the simplest model reactions and is being profitably applied to the analysis of processes in complex chemical systems, to heterogeneous catalysis, and to biological chemistry. That is why an intensive treatment of all new problems in the field of chain theory, the inner content of which is raised to the level of the general laws of the mechanism of many processes in nature, is so desirable.

CONCLUSION

Many properties and characteristic features of the chain-branching mechanism can serve as a basis for establishment of new principles of control of hydrocarbon oxidation processes. The tendency of degenerate chain-branching reactions of hydrocarbon oxidations in the liquid phase to be self-sustaining and self-accelerating enables us to effect their promotion ("elimination" of the induction period) by short-period treatment with gaseous initiators, penetrating radiations, salt catalysts, etc. in the initial period of development of the process.

In the homogeneous catalysis (induction) of hydrocarbon oxidation processes, a stagewise course of the reaction is frequently observed; this takes the form of consecutive macroscopic stages.

In some cases an analogous stepwise mechanism is also manifested in uncatalyzed oxidation. Addition of negative catalysts (inhibitors) can have different effects at different stages; the effect of addition of inhibitors to a starting mixture may therefore be markedly different from the effect when added to the reacting mixture. The existence of consecutive macroscopic stages enables us to control oxidation processes by changing the conditions in the course of the reaction when transition from one macroscopic stage to the next stage takes place.

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ADSORPTION EQUILIBRIA AND THE ENERGY OF ADSORPTION FORCES

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One of the most important problems of chemical thermodynamics is the determination of chemical equilibria. Such calculations, based upon the achievements of the theory of the chemical bond, the theory of heat capacity, thermochemistry, statistical thermodynamics and spectroscopic investigations of the state of reacting substances, enable us to determine chemical equilibria from the properties of the reactants without resorting to experimental examination of the equilibria. It is necessary to solve a similar problem for adsorption.

At the present time the determination of the adsorption equilibrium (adsorption isotherms) in any adsorbent — adsorbate system each time necessitates a fresh experimental study which is often very protracted and requires complex and delicate equipment. It is necessary to develop theoretical and experimental studies on the basis of which we could calculate the adsorptive properties of an adsorbent—adsorbate system, in particular the adsorption equilibria, with the help of other properties of adsorbent and adsorbate. The simplest case is the adsorption of gases on adsorbents with a homogeneous surface; in other cases complications are introduced by the chemical heterogeneity of the surface (presence at the surface of crystal faces with different indices and chemical modification of the surface), as well as by geometrical heterogeneity (uneven surface which may also be due to contraction of pores). Finally, the molecular fields in the gas phases must be taken into consideration in cases of adsorption from strongly compressed gases or from liquid solutions. Solution of these problems calls for detailed knowledge of the structure and properties of adsorption systems on the basis of which it would be possible to carry out calculations of the energy and entropy of adsorption required for calculation of the corresponding distribution functions, chemical potentials and equilibrium constants. Also of great auxiliary value is the development of methods of calculation of the adsorption properties of some adsorption systems from the known adsorption properties of other systems. One of the authors has already considered [1] these problems from a general aspect. In the present paper we consider only one of the important branches of these problems — the theoretical and experimental investigation of the energy of adsorption forces in physical adsorption of (mainly) complex, nonpolar molecules on adsorbents with an atomic and ionic lattice. Results of theoretical calculation are compared with measurements of differential heats of adsorption.

Energy of Adsorption as the Sum of the Energy of Interaction of the Energy Centers of a Molecule of Adsorbate and All of the Energy Centers of the Adsorbent

The wave function describing the reciprocal behavior of nuclei and electrons of a system of atoms, ions or molecules takes account of all "types" of their interaction; in the particular case of adsorption it also takes account of all types of adsorptive interactions. It is much more convenient, however, to treat the different types of interaction as independent [2]. In the present paper in considering the energy of adsorption of nonpolar molecules at low and ordinary temperatures, we introduced the forces of repulsion and attraction into the calculation; we also introduced dispersion forces in the case of adsorption on a nonpolar adsorbent, and dispersion and electrostatic forces (induction forces) in the case of adsorption on an adsorbent with an ionic lattice.

Important theoretical investigations of the energy of adsorption of simple (mono- and bivalent) nonpolar molecules were carried out as far back as the second half of the thirties by Barrer on graphite and by Orr on KCl and CsI. In calculating the energy of adsorption Barrer [3] started out from the Lennard-Jones "6, 12" potential:

$$\varphi = -Cr^{-6} + Br^{-12},$$ (1)

determining the constant of dispersive attraction from the Kirkwood formula and the repulsion constant from the condition for minimum φ-energy of interaction of a molecule of adsorbate with one atom of adsorbent at the equilibrium distance r_e; hence:

$$\varphi = -C\,(r^{-6} - 0.5\,r_e^6 r^{-12}).$$ (2)

Subsequently Barrer was the first to employ summation instead of integration [4] of the interactions of a molecule of adsorbate with individual atoms of adsorbent (with 100 atoms of the basal face of graphite), so that the energy of adsorption is expressed by:

$$\Phi = \sum_{}^{100} \varphi = -C\,\sum_{}^{100}(r^{-6} - 0.5\,r_e^6 r^{-12}).$$ (3)

Orr [5] calculated the dispersion potential in the same manner but introduced an exponential formula for the repulsion potential, as well as the induction potential in the form of one-half of the product of the polarizability and the square of the electrostatic field voltage in the center of the molecule of adsorbate, calculated by the procedure of Lennard-Jones and Dent [6]. Orr likewise employed summation of the interactions of the molecule of adsorbate with individual centers of the lattice of adsorbents. We calculated the adsorption energy of nitrogen, argon and krypton [7] and of hydrocarbons [8-11] on graphite by Barrer's procedure. Subsequently (report to the Second International Congress on Surface Activity in London [12]), however, we carried out summation of the Lennard-Jones 6-12 potential [1] not after but before determination of the repulsion constant B at the equilibrium distance r_e according to Formula (2), since a molecule of adsorbate is in equilibrium not with one atom of adsorbent but with all of its atoms.

In this work we calculated the repulsion potential Φ_R in the form of an exponential dependence on the distance r_{ij} of the adsorbed center $\underline{i}$ from the center of the lattice of adsorbent $\underline{j}$

$$\Phi'_{iR} = B'_i \sum_j e^{-r}{}_{ij}{}^{/\rho}$$ (4)

where the value of $\rho = 0.21$ A is that previously proposed for neon [13]. Putting the repulsion potential in the form of a power function

$$\Phi^{"}_{iR} = B^{*}_i \sum_j r_{ij}{}^{-m}$$ (5)

concordant results were obtained with m = 17.

In later calculations of the energy of adsorption on an ionic lattice [14], we calculated the constant ρ from the properties both of the adsorbate and the adsorbent according to the formula

$$\frac{1}{\rho} = \frac{1}{2}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right),$$ (6')

where ρ_1 and ρ_2 are, respectively, the constants for individual interactions of the components [15]. Moreover, the potential of dispersion forces in [14] took not only the first term containing r^{-6} (1) but also the following two terms containing r^{-8} and r^{-10} into account. In accordance with the latter procedure we now start out from the following theses: 1) the potential of the dispersive forces of attraction of a center $\underline{i}$ of a molecule of adsorbate to a lattice of adsorbent with centers $\underline{j}$ is expressed by a three-term equation

$$\Phi_{iD} = - C_{i1} \sum_j r_{ij}^{-6} - C_{i2} \sum_j r_{ij}^{-8} - C_{i3} \sum_j r_{ij}^{-10}, \tag{7}$$

2) the potential of the inductive forces of attraction is expressed by a relation between the polarizability center of a molecule of adsorbate α_i and the mean electrostatic field F created by the adsorbent at the site of this center $\underline{i}$

$$\Phi_{iJ} = - 0.5\alpha_i \bar{F}^2, \tag{8}$$

3) the relation between repulsion potential and the distance is expressed by exponential formula (4) where the constant ρ is governed by the respective individual constants of the adsorbent and adsorbate according to Eq. (6);
4) the equilibrium distance corresponds to the minimum of interaction energy Φ_i of the center $\underline{i}$ of a molecule of adsorbate with all the centers $\underline{j}$ of the lattice of adsorbent [and not to the energy of interaction φ with one of its centers as in (2)].

Energy of Adsorption of a Nonpolar Molecule on a Nonpolar Adsorbent

Relation between energy of adsorption and the geometrical properties of the adsorbent and the distance from its surface. In accordance with the foregoing considerations, the energy of adsorption of the center $\underline{i}$ of a molecule of adsorbate on a nonpolar adsorbent comprising $\underline{j}$ centers is:

$$\Phi'_i = - C_{i1} \sum_j r_{ij}^{-6} - C_{i2} \sum_j r_{ij}^{-8} - C_{i3} \sum_j r_{ij}^{-10} + B'_i \sum e^{-r_{ij}/\rho}, \tag{9'}$$

where the constants of dispersive attraction C_{i1}, C_{i2}, and C_{i3} are calculated theoretically, the constant ρ is calculated from Eq. (6'), and the repulsion constant B'_i is calculated from the condition for minimum of Φ_i at the equilibrium distance.

We see from Eq. (7) that the calculation of Φ_{iD} resolves itself into calculation of the constants of dispersive attraction C_{i1}, C_{i2} and C_{i3} and into calculation of the corresponding sums governed purely by the geometrical conditions of the adsorbent lattice structure which is usually well-known. Calculation of constants C_{i1}, C_{i2} and C_{i3} can only be carried out with approximation formulas. These formulas and the terms entering into them, which express the physical properties of adsorbent and adsorbate, can be later improved in precision. The geometrical sums were accordingly calculated separately from these constants in order that the values of the constants could be corrected with the help of known values of the sums which are only invested with small errors in the determination of the adsorbent lattice constants. In the case of the repulsion term the constant ρ is inserted under a summation sign; hence, the resolution of these factors is here impossible.

The summations entering into Eq. (9') can be conveniently expressed in the form of explicit functions of the distance $\underline{z}$ of the center $\underline{i}$ that is being adsorbed from the outer face of adsorbent xy (passing through the outer centers $\underline{j}$ of adsorbent). Summation of r_{ij}^{-6}, r_{ij}^{-8} and r_{ij}^{-10} were each effected at 250-100 centers $\underline{j}$, and for $e^{-r_{ij}/\rho}$ at 40-50 centers $\underline{j}$. The remaining volume of adsorbent was calculated by integration. This calculation was carried out for a series of values of $\underline{z}$. It was found that the relation between $\underline{z}$ and the values of the sums of the power functions of r_{ij} + the integrals could be expressed by the corresponding power functions of $\underline{z}$, while the relation between the values of $\Sigma e^{-r_{ij}/\rho}$ and $\underline{z}$ could be expressed as an exponential function of $\underline{z}$:

$$f_{D1}(z) = \left[\sum_\infty r_{ij}^{-6}\right](z) = \left[\sum^{r_1} r_{ij}^{-6}\right](z) + 2\pi\nu\left(\frac{1}{3r_1^3} - \frac{z}{4r_1^4}\right) = p_1 z^{-q_1}. \tag{10}$$

$$f_{D2}(z) = \left[\sum_\infty r_{ij}^{-8}\right](z) = \left[\sum^{r_2} r_{ij}^{-8}\right](z) + 2\pi\nu\left(\frac{1}{5r_2^5} - \frac{z}{6r_2^6}\right) = p_2 z^{-q_2}. \tag{11}$$

$$f_{D3}(z) = \left[\sum_{\infty} r_{ij}^{-10}\right](z) = \left[\sum^{r_3} r_{ij}^{-10}\right](z) + 2\pi\nu\left(\frac{1}{7r_3^7} - \frac{z}{8r_3^8}\right) = p_3 z^{-q_3}. \tag{12}$$

$$f_R'(z) = \sum e^{-r_{ij}/\rho} = ke^{-z/l} . \tag{13'}$$

Here r_1, r_2 and r_3 are the values of r_{ij} corresponding to the transition from summation to integration, and ν is the number of atoms of carbon in 1 cc of adsorbent. Consequently:

$$\Phi'_i(z) = -C_{i1}p_1 z^{-q_1} - C_{i2}p_2 z^{-q_2} - C_{i3}p_3 z^{-q_3} + B'_i ke^{-z/l} . \tag{14'}$$

The constants p_1, q_1, p_2, q_2, p_3 and q_3 were found from logarithmic graphs, and the constant l from the semilogarithmic curves of the dependence of the corresponding values of $\underline{f}$ on $\underline{z}$.

The relation between Φ_i and $\underline{z}$ (14') contains one unknown repulsion constant B'_i. Putting $\Phi_i(z)$ in the minimum form

$$\left(\frac{\partial \Phi_i(z)}{\partial z}\right)_{z=z_0} = 0, \tag{15}$$

where z_0 corresponds to the equilibrium distance of a center $\underline{i}$ from the plane xy, we find B'_i and express it in terms of the remaining constants and z_0:

$$B'_i k = \left[C_{i1}p_1 \frac{q_1 l}{z_0} z_0^{-q_1} + C_{i2}p_2 \frac{q_2 l}{z_0} z_0^{-q_2} + C_{i3}p_3 \frac{q_3 l}{z_0} z_0^{-q_3}\right]\cdot e^{z_0/l} \tag{16'}$$

Substituting (16') in (9'), we obtain the expression for plotting of the potential curve:

$$\Phi'_i(z) = -C_{i1}p_1 z^{-q_1} - C_{i2}p_2 z^{-q_2} - C_{i3}p_3 z^{-q_3} + $$
$$+ \left(\frac{q_1 l}{z_0}C_{i1}p_1 z_0^{-q_1} + \frac{q_2 l}{z_0}C_{i2}p_2 z_0^{-q_2} + \frac{q_3 l}{z_0}C_{i3}p_3 z_0^{-q_3}\right) e^{\frac{z_0-z}{l}} . \tag{17'}$$

At the minimum of this curve (when $z = z_0$) the energy of adsorption is:

$$\Phi'_{i0} = -\left(1 - \frac{q_1 l}{z_0}\right)C_{i1}p_1 z_0^{-q_1} - \left(1 - \frac{q_2 l}{z_0}\right)C_{i2}p_2 z_0^{-q_2} - \left(1 - \frac{q_3 l}{z_0}\right)C_{i3}p_3 z_0^{-q_3}. \tag{18'}$$

Analogous expressions can also be obtained by using the power dependence of the repulsion potential on r_{ij} (5). In this case

$$f_R''(z) = \left[\sum_{\infty} r_{ij}^{-m}\right](z) = \left[\sum^{r_m} r_{ij}^{-m}\right](z) + 2\pi\nu\left(\frac{1}{(m-3) r_m^{m-3}} \frac{z}{(m-2) r_m^{m-2}}\right) = p_m z^{-q_m}, \tag{13''}$$

Here the constant q_m was found from the logarithmic plot of the dependence on $\underline{z}$ of the values of $f_R''(z)$ calculated for different values of $\underline{z}$. Hence:

$$\Phi''_i(z) = -C_{i1}p_1 z^{-q_1} - C_{i2}p_2 z^{-q_2} - C_{i3}p_3 z^{-q_3} + B''_i p_m z^{-q_m}. \tag{14''}$$

From the equilibrium condition (15)

$$B_i'' p_m = \left[C_{i1} p_1 \frac{q_1}{q_m} z_0^{-q_1} + C_{i2} p_2 \frac{q_2}{q_m} z_0^{-q_2} + C_{i3} p_3 \frac{q_3}{q_m} z_0^{-q_3} \right] z_*^{q_m} . \tag{16"}$$

The dependence of Φ_i'' on $\underline{z}$ acquires the form

$$\Phi_i''(z) = - C_{i1} p_1 z^{-q_1} - C_{i2} p_2 z^{-q_2} - C_{i3} p_3 z^{-q_3} +$$

$$+ \left[C_{i1} p_1 \frac{q_1}{q_m} z_0^{-q_1} + C_{i2} p_2 \frac{q_2}{q_m} z_0^{-q_2} + C_{i3} p_3 \frac{q_3}{q_m} z_0^{-q_3} \right] z^{-q_m} z_0^{q_m} , \tag{17"}$$

and the adsorption energy at the equilibrium distance $z = z_0$ becomes

$$\Phi_{i0}'' = - \left(1 - \frac{q_1}{q_m}\right) C_{i1} p_1 z_0^{-q_1} - \left(1 - \frac{q_2}{q_m}\right) C_{i2} p_2 z_0^{-q_2} - \left(1 - \frac{q_3}{q_m}\right) C_{i3} p_3 z_0^{-q_3}. \tag{18"}$$

In our calculations Formulas (18') and (18") replaced Barrer's formula (3).

Results of calculations of the sums and integrals for different values of $\underline{z}$ for specific cases are presented by us in separate papers [14, 16].

Dependence of the adsorption energy on the physical properties of adsorbent and adsorbate. We have already considered the method of calculation of the repulsion constant ρ in Eq. (4) from the corresponding constants of the adsorbent and adsorbate (6'). The repulsion constant $\underline{m}$ in Eq. (5) can be similarly evaluated if the repulsion potential is expressed by the power function

$$m = \frac{1}{2}(m_1 + m_2). \tag{6"}$$

The twelfth power of the distance is taken for repulsion in the Lennard-Jones potential for individual substances. In addition, therefore, to calculate Φ' through the exponential law for the repulsion potential (6'),for comparison we also calculated Φ'' by the power relation for repulsion in the case of m = 12.

The constants of dispersive attraction can be calculated by a different procedure [2, 17]. For molecules with many electrons these constants can be expressed through the mean polarizabilities and diamagnetic susceptibilities of the respective molecules (or their nonpolar segments) and the adsorbent centers. Thus, we calculated the first dispersion constant from Kirkwood's equation [18]:

$$C_{i1} = - 6mc^2 \alpha_i \alpha_j \frac{1}{\alpha_j / \chi_j + \alpha_i / \chi_i} . \tag{19}$$

For the subsequent constants we can obtain analogous expressions [14, 17, 19]:

$$C_{i2} = \frac{45h^2}{32\pi^2 m} \alpha_i \alpha_j \left[\frac{1}{2\left(\frac{\alpha_j}{\chi_j} \bigg/ \frac{\alpha_i}{\chi_i}\right) + 1} + \frac{1}{2\left(\frac{\alpha_i}{\chi_i} \bigg/ \frac{\alpha_j}{\chi_j}\right) + 1} \right], \tag{20}$$

$$C_{i3} = - \frac{105h^4}{256\pi^4 m^3 c^2} \alpha_i \alpha_j \left[\frac{\alpha_i / \chi_i}{3\left(\frac{\alpha_j}{\chi_j} \bigg/ \frac{\alpha_i}{\chi_i}\right) + 1} + \frac{3}{4} \frac{1}{\frac{\chi_i}{\alpha_i} + \frac{\chi_j}{\alpha_j}} + \frac{\alpha_j / \chi_j}{3\left(\frac{\alpha_i}{\chi_i} \bigg/ \frac{\alpha_j}{\chi_j}\right) + 1} \right]. \tag{21}$$

In these expressions α_i and χ_i are the polarizability and susceptibility of the center $\underline{i}$ of a molecule of adsorbate; α_j and χ_j are the same for a center $\underline{j}$ of the adsorbent; $\underline{m}$ is the electron mass; $\underline{c}$ is the velocity of light, and $\underline{h}$ is the Planck constant.

The energy of adsorption of a complex molecule consisting of several energy centers i (atoms, groups of atoms, segments of a hydrocarbon chain), is expressed, as we showed in [8, 10-12], by an additive function of the adsorption energies of individual centers

$$\Phi = \sum_i \Phi_i, \tag{22}$$

since the polarizabilities and susceptibilities of many molecules (such as molecules of hydrocarbons) are additive functions of this type.

Energy of Adsorption of a Nonpolar Molecule on an Ionic Adsorbent

In this case the energy of the inductive forces of attraction is superposed on the energy of the dispersive forces; the potential of the former was calculated from Eq. (8). The electrostatic field F is heterogeneous but small, especially in the case of alternating arrangement of the ions at the adsorbed face of an ionic crystal, for example, at the (100) face of simple cubic lattices. Taking into consideration the heterogeneity of this field, we introduced into Eq. (8) the mean value of the squares of the maximum and minimum field [14]

$$\overline{F^2} = \frac{1}{2}\left(F_{max}^2 + F_{min}^2 \right). \tag{23}$$

For the (100) face the field potential F was calculated by Lennard-Jones and Dent [6], from which $F_{min} = 0$ (intermediate between the ions*) and

$$F_{max} = \frac{8\pi v \epsilon}{d^2 (1 + e^{-\sqrt{2}\cdot\pi})} e^{-\frac{\sqrt{2}\cdot\pi}{d}\cdot z}, \tag{24}$$

where v is the valence of the ion; ϵ is the electronic charge; and d is the lattice constant. Putting $\frac{16\pi^2 v^2 \epsilon^2}{d^4 (1 + e^{-\sqrt{2}\cdot\pi})^2}\alpha_i = A_i$ and $\frac{2\sqrt{2}\cdot\pi}{d} = a$, we obtain the energy of the inductive forces on adsorption in the form of an exponential function of z

$$\Phi_{iJ} = -A_i e^{-az}. \tag{25}$$

For calculation of the total energy of adsorption Φ_i this term was added to Eqs. (14') or (14"), after which the repulsion constants $B_i'k$ in (14') or $B_i''p_m$ in (14") were calculated from the equilibrium condition of (15) through the dispersive attraction constants C_{i1}, p_1, q_1, C_{i2}, p_2, q_2, C_{i3}, p_3, q_3, the repulsion constants l or q_m, the distance z_0, as well as through the new inductive attraction constants A_i and a. For the adsorption energy $\Phi_i'(z)$ when $z = z_0$ this gives, for example, [14]:

$$\Phi'_{i0} = -\left(1 - \frac{q_1 l}{z_0}\right) C_{i1} p_1 z_0^{-q_1} - \left(1 - \frac{q_2 l}{z_0}\right) C_{i2} p_2 z_0^{-q_2} -$$
$$-\left(1 - \frac{q_3 l}{z_0}\right) C_{i3} p_3 z_0^{-q_3} - (1 - al) A_i e^{-az_0}. \tag{26}$$

Energy of Adsorption in the Case of Standard Coverage of the Surface

The above calculations give the energy of adsorption of individual molecules on a homogeneous surface. The energy of adsorption in the case of standard coverage of an adsorbent surface enters into calculations of the equilibrium constants to the extent of one-half, $\theta = 0.5$ [8, 9, 11, 12]. In addition, comparison with heats of

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* Another method of taking this field and the polarizability of the molecule of adsorbate into account [20] does not lead to results differing substantially in the quantitative respect.

adsorption is frequently more conveniently effected not with $\theta = 0$ but with larger coverages, since in the region of small coverages the residual heterogeneity of the surface usually increases the heats of adsorption. For conversion of Φ_0 from $\theta = 0$ to $\theta = 0.5$ it is necessary to take into consideration the energy of interaction between molecules of adsorbate in the adsorption layer. On surfaces of nonpolar adsorbents and on surfaces of ionic adsorbents with alternating ions of opposite signs between molecules of adsorbate, the attractive forces predominate [14]. When $\theta = 0.5$, the mean of the distance between the centers of these molecules is usually quite large (of the order of 10 A). For the purpose of determination of the relatively small correction to Φ_0^* at such distances, it suffices to consider the energy of interaction with the closest neighbors which can be easily calculated as the energy of dispersive attraction between two molecules multiplied by the number of closest neighbors N. In this manner the standard energy of adsorption can be written:

$$\Phi^0 = \Phi_0 - NCr_{\theta \to 0.5}^{-6},\tag{27}$$

where C is the dispersion constant of the adsorbate, and $r_{\theta=0.5}$ is the mean distance between the centers of molecules of adsorbates when $\theta = 0.5$. The magnitudes of $NCr_{\theta=0.5}^{-6}$ are usually less than 2-5% of Φ_0.

The problem of the influence of temperature on the energy of adsorption is fairly complicated [10]. In the calculations set forth above, the only temperature-dependent factors are the geometrical factors associated with the adsorbent lattice parameters and the van der Waals dimensions of molecules of adsorbates; these terms alter but little with the temperature. The orientation of molecules of adsorbate relative to the lattice is very important for the employment of the derived equations in practice. With change of temperature these orientations can change from a position with maximum Φ to positions with minimum Φ. Investigations of adsorption entropies are necessary in order to establish the magnitude of this effect. Also necessary are investigations of the heats of adsorption at different temperatures and in particular investigations of the heat capacities of adsorption systems. Existing measurements show that the heat of adsorption on a nonpolar adsorbent (active carbon) is substantially independent of the temperature [21].

Energy of Adsorption Forces and Heat of Adsorption on Graphite

Choice of constants. We considered adsorption on the basal face and assumed the following values for the lattice constants: distance between neighboring atoms in the basal plane a = 1.418 A; distance between adjacent basal planes c = 3.395 A.** On the basis of these values, the magnitudes of $f_{D1}, f_{D2}, f_{D3}, f_R^*$ and f_R^{**} were calculated for values of $\underline{z}$ equal to 2.0 a, 2.5 a, 3.0 a and 3.5 a.*** Detailed results of these calculations appear in another publication [23].

The repulsion constant ρ of benzene is 0.28 A [24]. This value of ρ was accepted for graphite and for all graphite—hydrocarbon systems (6'), as well as for neon, argon, krypton and nitrogen [19]. The constant $\underline{m}$ for these systems was assumed to be 12 (Lennard-Jones).

The polarizability and susceptibility of graphite have been taken as $\alpha_j = 0.937 \cdot 10^{-24}$ cc and $\chi_j = 10.54 \cdot 10^{-30}$ cc [3]. Mean values of α_i and χ_i were taken for molecules of adsorbates or their increments. The contributions of the second and third terms of the dispersive interaction (dipole-quadrupole and quadrupole-dipole) amount, respectively, to $\sim 5\text{-}10$ and $0.5\text{-}1\%$ of the contribution of the total energy of the dispersive forces (7). The absolute magnitude of the energy of the repulsive forces (4) is $\sim 35\text{-}40\%$ of the total magnitude of the energy of the dispersive forces (7).

Following Barrer [3], we calculated the values of Φ_0^* and Φ_0^{**} for three different positions of a molecule or a segment of a molecule of adsorbate $\underline{i}$ relative to the adsorbent centers $\underline{j}$ (atoms of carbon of the basal face): over an atom of carbon Φ_c, over the center of the hexagon of these atoms Φ_h, and over the mean distance between

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* A more accurate method is necessary if the main problem is not calculation of interaction with adsorbent but rather that of interaction between molecules of adsorbate.

** This distance may possibly be different between an external and an adjacent plane [5, 22], but this should not introduce a serious error because the magnitude of Φ is governed to a substantial extent by the centers of the outer basal plane.

*** The values of f_{D1} and f_R^{**} that we obtained agree with those cited in [23].
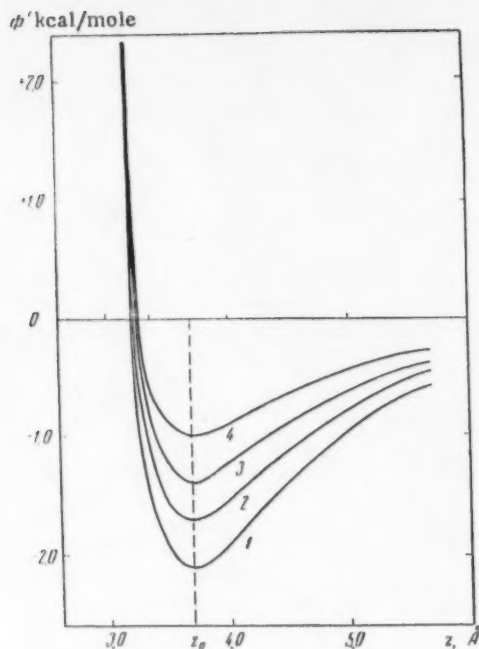
ϕ'kcal/mole

Fig. 1. Potential curves for adsorption of segments of alkanes CH_3 (1), CH_2 (2), CH (3) and C (4) in position over a carbon atom. The contribution of both of the H centers in CH_2 is assumed to be identical [8].

two closest atoms (over the middle of the bisector) Φ_b. The first position is energetically the least favorable; the second is energetically the most favorable. In the position over a carbon atom, the equilibrium distance z_{0C} is assumed equal to r_e — the sum of the van der Waals radius of the corresponding center of the molecule of adsorbate and one-half of the interplanar distance in graphite; these are, respectively, $z_{0b} = \sqrt{r_e^2 - 0{,}25a^2}$ and $z_{0h} = \sqrt{r_e^2 - a^2}$. . Errors in the value of r_e of 0.1 A can change Φ by approximately 10% [8]. Examples of the potential curves for adsorption on graphite of CH_3, CH_2, CH and C segments of a molecule of alkane with z_0 = 3.70 A, calculated from Eq. (17'), are plotted in Fig. 1.

Differential heats of adsorption of vapors on graphitized carbon blacks. It is interesting to compare the results of calculation of the energy of adsorptive forces with corresponding measurements of differential heats of adsorption. Beebe and co-workers [25-27], Aston and Greyson [28] and Ross and Winkler [29] have published reliable values of the heats of adsorption of a series of noble gases and nitrogen on carbon blacks graphitized at high temperatures and possessing an extremely homogeneous surface. The narrow range of the initial fall in differential heat of adsorption Q_a, the gradual rise of Q_a toward the end of the monolayer, and the sharp fall in Q_a on transition to predominant adsorption in the second layer bear witness to the high degree of homogeneity of the surface of graphitized carbon blacks. Carbon black P-33, graphitized at 2700°, has a particularly homogeneous surface. For this material a participation of the initial pressure Q_a is not observed [27]. The magnitudes of the heats of adsorption in the middle region θ are substantially unchanged with rising temperature of graphitization above 1500° [26]. For such carbons, the values of Q_a at θ = 0 can therefore be considered sufficiently reliable when the middle portion of the Q_a/θ curve is extrapolated to θ = 0.

Heats of adsorption of complex molecules are of particular interest. Using a constant heat-exchange calorimeter, we investigated the differential heats of adsorption of vapors of eleven hydrocarbons (n-alkanes, iso- and neoalkanes, cyclanes and aromatics) on Spheron-6 carbon black graphitized at 1700° in hydrogen [8, 9, 11, 12, 30]. Beebe and co-workers measured the heats of adsorption of 1-butene and n-butane on Graphon carbon black [31]. Ross and Good determined the isosteric heat of adsorption of n-butane on carbon black P-33 graphitized at 2700° [32]. Results of our measurements are plotted in Fig. 2.

We see from Fig. 2 that the standard values of the differential heats of adsorption Q_a^0 at θ = 0.5 can be determined with great accuracy from these data. These data also permit sufficiently reliable determination of Q_a when θ = 0 by extrapolation of the middle portion of the Q_a/θ curves in the region of monomolecular coverage to θ = 0. *

Results of calculation of the energy of adsorptive forces on graphite and their comparison with measured heats of adsorption on graphitized carbon blacks. Table 1 contains the values of heats of adsorption (for θ = 0) and results of calculation of the energy of adsorptive forces for various positions of simple molecules relative to the centers of the basal face of graphite.

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* Part of the kinetic energy of a molecule may be released in the form of heat (usually 0.5 RT or RT) on transition from the gas phase to the adsorption layer, so that the measured heats of adsorption may slightly exceed the corresponding value of Φ. Knowledge of the state of molecules in the adsorption layer is necessary to enable us to make the correction [33].
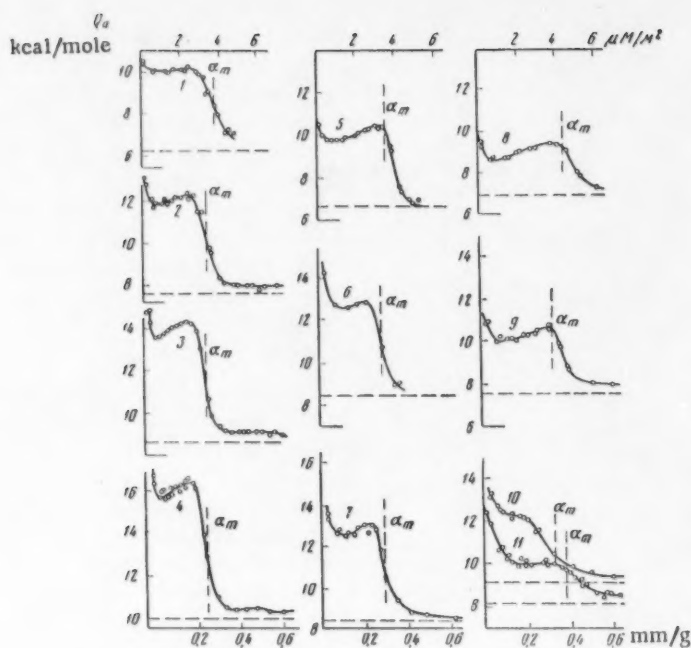
Fig. 2. Differential heat of adsorption on graphitized carbon black as a function of the quantity of adsorbed hydrocarbon vapor: n-pentane (1), n-hexane (2), n-heptane (3), n-octane (4), 2,2-dimethylbutane (5), 3-methylhexane (6), 2,2,4-trimethylpentane (7), cyclopentane (8), methylcyclopentane (9), toluene (10), and benzene (11). Dashed horizontal lines are heats of condensation L; dashed vertical lines are volumes of monolayers α_m.

We see from the table that the measured heat of adsorption lies in the range of calculated values of $\overline{\Phi_0'}$ (from the "6, 8, 10; $e^{-r/0.280}$" potential) for different positions. The magnitudes of $\overline{\Phi_0''}$ (from the "6, 8, 10, 12" potential) are close to the values of $\overline{\Phi_0'}$.*

The energy of adsorption of n-alkanes was calculated according to (22) as an additive function of the energies of adsorption of the CH_3 and CH_2 segments [8]:

$$\Phi = 2\Phi_{CH_3} + (n - 2)\,\Phi_{CH_2} = 2\,(\Phi_{CH_3} - \Phi_{CH_2}) + n\Phi_{CH_2} = a + bn. \tag{28}$$

It is a linear function of the number of carbon atoms $\underline{n}$.

Table 2 contains values of the increments of the energy of adsorption of CH_3 and CH_2 and the corresponding increments of the heats of adsorption calculated from (18') and (18"); in Fig. 3 the calculated dependence of the mean value $\overline{\Phi_0'}$ for different positions of n-alkanes is plotted against $\underline{n}$; the points are heats of adsorption. The

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* Comparison of the results of calculation of other authors [3, 2, 34, 29] is given by us in [7]. In [35] are presented the results of calculation of the energy of adsorption of noble gases on graphite on the assumption of uninterrupted surface of carbon in each plane. They are slightly low and close to our calculated values for the position over an atom of carbon. Results were obtained in [34] for other positions which were close to those obtained for the position over a carbon atom. This is presumably because identical values of $z_{0c} = z_{0b} = z_{0h} = r_e$ were assumed in [34] for all positions whereas for positions over the center of a hexagon and over a bisector smaller values of z_{0h} and z_{0b} correspond to the same value of r_e, so that the adsorption energy is increased.

TABLE 1

Comparison of Results of Theoretical Calculation of the Energy of Adsorption (When $\theta = 0$) for Three Different Positions Φ'_{0c}, Φ'_{0b}, and Φ'_{0h} and of the Mean Values $\overline{\Phi'_0}$ and $\overline{\Phi''_0}$ with the Experimental Heats of Adsorption $Q_{a=0}$ (kcal/mole)

Adsorbate	$Q_{a=0}$	Φ'_{0c}	Φ'_{0b}	Φ'_{0h}	$\overline{\Phi'_0}$	$\overline{\Phi''_0}$
Neon	0.85 [28]	0.81	0.87	1.12	0.93	0.91
Argon	2.6 [26]; 2.27 [29]	2.14	2.26	2.82	2.41	2.22
Krypton	3.9 [27]; 3.24 [29]	2 92	3.06	3.78	3.25	2.95
Nitrogen	2.7 [25]; 2.19 [29]	2 14	2.27	2.89	2.43	2.30

TABLE 2

Comparison of Results of Theoretical Calculation of the Energy of Adsorption of Hydrocarbons on Graphite for Three Different Positions Φ'_{0c}, Φ'_{0b}, and Φ'_{0h} and Mean Values of $\overline{\Phi'_0}$ and $\overline{\Phi''_0}$ with Experimental Values of Heats of Adsorption Q_a When $\theta = 0$ (kcal/mole)

Adsorbate	$Q_{a=0}$	Φ'_{0c}	Φ'_{0b}	Φ'_{0h}	$\overline{\Phi'_0}$	$\overline{\Phi''_0}$
CH_3 in n-alkane	2.30	2.10	2.20	2.73	2.31	2.09
CH_2 in n-alkane	1.80	1.69	1.77	2.19	1.88	1.71
n-Butane	8.6 [31] 8.2 [32]	7.5	7.8	9.7	8.3	7.6
n-Pentane	10.0	9.2	9.6	11.9	10.2	9.3
n-Hexane	11.8	10.9	11.4	14.3	12.2	11.0
n-Heptane	13.6	12.6	13.6	15.4	14.0	12.7
n-Octane	15.5	14.2	14.9	18.5	15.9	14.4
2,2-Dimethylbutane	9.4	9.0	9.6	11.5	10.0	9.2
3-Methylhexane	12.5	11.7	12.3	15.0	13.0	11.9
2,2 4-Trimethylpentane	12.5	11.2	11.8	14.3	12.4	11.3
1-Butene	8.2 [31]	6.5	6.9	8.5	7.3	6.6
Cyclopentane	8.6	8.4	8.9	11.0	9.4	8.6
Methylcyclopentane	9.9	9.2	9.6	11.9	10.2	9.3
Benzene	10.0	10.1	10.6	13.4	11.4	10.6
Toluene	12.1	11.8	12.1	15.6	13.2	12.3

calculated values of $\overline{\Phi'_0}$ and the measured heats of adsorption $Q_{a=0}$ for five n-alkanes are also compared in Table 2. We see from this table and from Fig. 3 that the values of $Q_{a=0}$ lie within the range calculated for various positions of the values of Φ'_0, and are very close to the mean value of $\overline{\Phi'_0}$:

$$-\overline{\Phi'_0} = 0.85 + 1.88\,n \ \text{kcal/mole}, \tag{28'}$$

since the individual segments of a molecule of an n-alkane can be located in different positions relative to the basal face of graphite.* Calculation of Φ''_0 (from the "6, 8, 10, 12" potential) leads to somewhat lower values.

Certain difficulties arise in the calculation of the energy of adsorption of isomeric alkanes by an additive scheme because for segments of their molecules with large separation distance from the surface the attraction is greater than the repulsion. In practice this is compensated by the slightly greater repulsion of the parts of the molecule closest to the surface. We used an additive scheme for the calculation, determining the potential curve of the molecule on the basis of the increments of the energy of adsorption of individual segments from potential curves calculated by (17') and (17").

* The corrections introduced show that our previously obtained formula [8, 10, 11]

$$-\Phi_0 = 0.9 + 1.85\,n \ \text{kcal/mole} \tag{29}$$

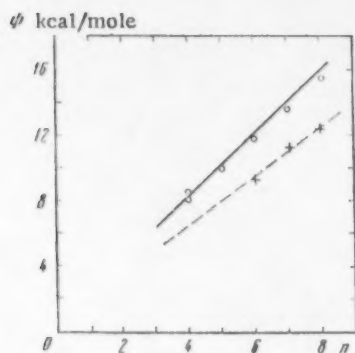is a sufficiently close approximation.

ψ kcal/mole

Fig. 3. Dependence of the theoretically calculated energy of adsorption of n-alkanes $\overline{\Phi_0'}$ on graphite for the case of $\theta = 0$ (continuous line) and $\overline{(\Phi')}^{\circ}$ on MgO for the case of $\theta = 0.5$ (dashed line). The circles relate to experimental data for $Q_{a=0}$ ($\theta = 0$) on graphitized carbon black; the crosses relate to data for Q_a^0 on MgO.

The energy of adsorption of cyclopentane is equal to the energy of adsorption of five CH_2 groups of n-alkanes. We see from Table 2, however, that the measured heat of adsorption is close not to the mean value of $\overline{\Phi_0'}$ for the three positions but to the magnitude of Φ_{0C} corresponding to the position of the CH_2 segments above the atoms of carbon. This corresponds to a plane structure of the molecule of cyclopentane whose individual segments, in contrast to the segments of n-alkanes, cannot pile up into more favorable positions above the centers of hexagons. This also happens in the case of adsorption of the plane benzene ring.

The energy of adsorption of benzene on graphite was calculated from the mean value of its polarizability and susceptibility. We may note that in the case of adsorption on graphite not complicated by supplementary interactions of the donor—acceptor type, as in the adsorption on acidic adsorbents [36], the energy of adsorption of benzene is smaller than the energy of adsorption of n-hexane (an alkane with the same number of carbon atoms).

For calculation of the energy of adsorption of toluene, we should take the difference between the contribution of the hydrogen of the aromatic ring and of the CH_3 group into consideration. This difference, however, is small, and therefore we calculated the energy of adsorption of toluene as the sum of the energies of adsorption of benzene and the CH_2 group of n-alkanes.

We calculated the energy of adsorption of α-monoolefins by adding the energy of adsorption of the $CH_2 = CH$ group and the normal aliphatic radical. This gives a linear relation between Φ and $\underline{n}$:

$$\Phi = \Phi_{CH_2-CH} + (n-3)\Phi_{CH_2} + \Phi_{CH_3} = \Phi_{CH_2-CH} + \Phi_{CH_3} - 3\Phi_{CH_2} + n\Phi_{CH_2} \qquad (30)$$

$$-\overline{\Phi_0'} = -0.2 + 1.88n \quad \text{kcal/mole} \qquad (30')$$

The calculated values for 1-butene are also given in Table 2.

The data presented in Fig. 3 and Table 2 show that the calculation of the energy of adsorption of hydrocarbons on graphite, starting from the "6, 8, 10; $e^{-r} {}^{0.28}$" potential, gives results extremely close to the experimental heats of adsorption.

Energy of Adsorption Forces and Heat of Adsorption of Hydrocarbons on Magnesia

Choice of constants. We have examined adsorption on the (100) face. The lattice constant $\underline{d}$ is assumed to be 2.1 A. Detailed results of calculations of f_{D1}, F_{D2}, f_{D3}, f_R' and f_R'' for various values of $\underline{z}$ are reported in another paper [14]. For adsorption of hydrocarbons z_0 is taken as identical for all positions and equal to the sum of the van der Waals radius of the corresponding segment of a molecule of adsorbate and half of $\underline{d}$. Polarizabilities and susceptibilities of the ions were taken as equal, respectively, to $\alpha_{Mg}++ = 0.11 \cdot 10^{-24}$, $\alpha_O-- = 1.69 \cdot 10^{-24}$; $x_{Mg}++ = -6.7 \cdot 10^{30}$ and $x_O-- = -10 \cdot 10^{-30}$ cc [14]. The repulsion constant $\rho = 0.31$ A was obtained from Formula (6') from the value $\rho = 0.28$ A for hydrocarbons and $\rho = 0.34$ A for ionic crystals [37]. In a formula with a power function of the repulsion potential, it was assumed that m = 12. Allowance was made for the contribution of the inductive forces (26) in the calculation by introduction into (25) of the mean of the polarizability of the adsorbates.

The contributions of the first, second and third terms of the energy of dispersive forces, energy of inductive forces and the absolute magnitude of the repulsion energy constitute about 81-83; 12-14; 3; 2 and 42-48%, respectively, of the total energy of the attractive forces (dispersive and inductive).
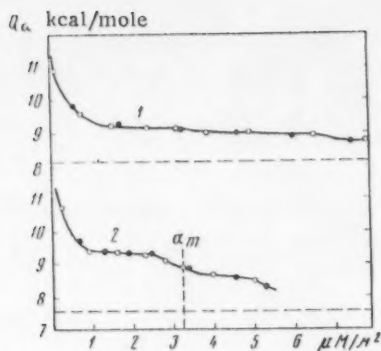
q_α kcal/mole

Fig. 4. Differential heat of adsorption of MgO as a function of the quantity of hydrocarbon adsorbed: benzene (1) and n-hexane (2). Horizontal broken lines relate to heats of condensation L; vertical broken line relates to the volume of the monolayer α_m; black points denote desorption.

Differential heats of adsorption of vapors of MgO were calculated for $\theta = 0.5$ from the isosteres of Shreiner and Kemball for adsorption of n-heptane, benzene and toluene [38]. We determined the differential heats of adsorption on MgO of the vapors of n-hexane, n-octane and benzene in a calorimeter with constant heat-exchange described in [39]. We prepared magnesia by calcination of extremely large-pore preparations of $Mg(OH)_2$ in vacuum at $1000°$ [40, 41]. Results are plotted in Fig. 4; they enable reliable determination of the standard heat of adsorption Q_a^0. The magnitude of Φ was therefore likewise calculated from Formula (27) for $\theta = 0.5$.

Results of calculation of the energy of adsorptive forces on MgO and their comparison with the measured heats of adsorption. In Table 3 are set forth the values of $(\overline{\Phi'})^0$, $(\overline{\Phi''})^0$ and Q_a^0 (for $\theta = 0.5$). For n-alkanes the calculation gives the linear relation:

$$- (\overline{\Phi'})^0 = 0.90 + 1.39\,n \quad \text{kcal/mole} \tag{31'}$$

$$- (\overline{\Phi''})^0 = 0.94 + 1.50\,n \quad \text{kcal/mole} \tag{31''}$$

TABLE 3

Comparison of Results of Theoretical Calculation of the Energy of Adsorption of Hydrocarbons on MgO $(\overline{\Phi'})^0$ and $(\overline{\Phi''})^0$ (for $\theta = 0.5$) with the Experimental Values of the Heats of Adsorption Q_a^0 kcal/mole

Adsorbate	Q_a^0	$(\overline{\Phi'})^0$	$(\overline{\Phi''})^0$
n-Hexane	9.4	9.2	9.9
n-Heptane	11.3 [38]	10.6	11.4
n-Octane	12.4	12.0	12.9
Benzene	9.2; 9.1 [38]	8.4	9.3
Toluene	10.3 [38]	9.8	10.8

In Fig. 3 the calculation by means of Formula (31') is compared with the heats of adsorption. We see from Fig. 3 and Table 3 that the energy of adsorption of hydrocarbons on magnesia is less than the energy of adsorption on graphite (in spite of the additional contribution of the inductive forces of attraction) due to the lower energy of the dispersive forces. In this case again, the calculated values of the energy of the adsorptive forces are close to the measured adsorption heats.

SUMMARY

1. The adsorption energy of nonpolar molecules is calculated by a method which takes into consideration three terms in the potential of the dispersive forces by means of constants calculated on the basis of the polarizabilities and magnetic susceptibilities. Other factors taken into consideration in the development of the method are inductive potential (through the mean polarizability of the adsorbate and the mean electrostatic field of the adsorbent) and the repulsion potential (through an exponential constant calculated from the individual constants of adsorbent and adsorbate and with summation of all of the interactions of the given energy center of the molecule of adsorbate over all of the centers of the lattice of the adsorbent). The exponential repulsion constant was determined from the minimum condition of the summed energy of all of the interactions at the equilibrium distance from the adsorbent surface.

2. The calculated values of the energy of adsorption of noble gases, nitrogen and thirteen hydrocarbons of various structures (normal and isomeric alkanes, an alkene, cyclanes and aromatics) on graphite are close to the measured heats of adsorption on graphitized carbon blacks.

3. The calculated values of the energy of adsorption of n-alkanes, benzene and toluene on magnesia are likewise close to the measured heats of adsorption.

4. In the case of adsorption on graphite the contributions of the first, second and third terms of the energy of the dispersive forces and the absolute value of the repulsion energy constitute 90-95, 5-10, 0.5-1 and 35-40%, respectively, of the total energy of the dispersive forces for the investigated adsorbates.

In the case of adsorption of MgO the contributions of the first, second, and third terms of the energy of the dispersive forces, the energy of the inductive forces and the absolute magnitude of the repulsion energy constitute about 81-83, 12-14, 3, 2 and 42-48%, respectively, of the total energy of the attractive forces (dispersive and inductive).

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INVESTIGATION OF THE VAPOR-PHASE HYDROLYSIS OF CHLOROBENZENE IN PRESENCE OF A PHOSPHATE CATALYST

L. Kh. Freidlin, A. A. Balandin, and G. A. Fridman

The choice of catalysts for the vapor-phase hydrolysis of aryl halides has been the subject of many investigations. Dozens of substances have been tested as catalysts — metals, their oxides, salts and acids. It was found that in the absence of promoters silica gel is the only substance that accelerates this reaction. The activity of some of the substances mentioned in the literature is undoubtedly also due to their content of polysilicic acid [1]. Only a few other substances manifest catalytic activity in this reaction. Small and short-lived activity is exhibited, for example, by stannic [2], titanic [2, 3] and aluminic acids [4]. In their presence the yield of phenol from chlorobenzene at 450-500° is less than 1% of the theoretical but can be slightly increased by promotion with copper chloride. The selectivity of these catalysts is also poor (the yield of hydrochloric acid considerably exceeds the yield of phenol). In the absence of catalysts, however, chlorobenzene generally does not react with water under the same conditions.

All these and a number of other facts are satisfactorily explained by our earlier theory to the effect that in the process of vapor-phase hydrolysis on silica gel there is surface interaction of the aryl halide with the silica gel which then functions as a weak but thermally stable acid [5]. This theory also accounts for the difficulty of selection of catalysts for this reaction. It appears that hardly any compounds are known that resemble silica gel in exhibiting weakly acidic properties, in being stable under the conditions of a high-temperature reaction and in satisfying the theoretical requirements of a catalyst in this reaction. Detailed consideration of a model of a catalyst for the vapor-phase hydrolysis of aryl halides has appeared in previous publications [1, 5].

It is therefore natural that interest should be aroused by the reports of the catalytic activity of phosphate catalysts whose composition and properties are only briefly described in the literature. Catalysts for vapor-phase hydrolysis of chlorobenzene at 350-700° recommended in patents are neutral and acid manganese pyrophosphates and their mixtures with copper [6], calcium phosphate [7] and other phosphates of the alkaline-earth metals on which are deposited Cu, Ni, Co, Ag, Au or metals of the Pt group [8], salts, oxides or hydroxides of metals on which copper phosphate or zinc phosphate is deposited [9]. It is claimed that the yield of phenol in the reaction reaches 90% of the theoretical. In the same manner as chlorobenzene, chloro derivatives of toluene, naphthalene, diphenyl, etc. are hydrolyzed on phosphate catalysts. Phosphate catalysts have been tested in a pilot plant in Germany [10].

Our investigations show that tricalcium phosphate is likewise an active catalyst for this reaction and is comparable with silica gel. The probable similarity in the mechanism of their activating action may be attributed to the acidic character of both catalysts.

EXPERIMENTAL

The experimental procedure for this investigation was the same as that formerly employed with a silica gel catalyst [11]. The reaction was carried out by a flow method. An approximately 1 : 1 ratio (by weight) of water to chlorobenzene was maintained in all of the experiments. The duration of an experiment was 1-2 hrs. The space velocity was 300 g of chlorobenzene per liter of catalyst per hr. Yields of acid and phenol are given in percentages of the theoretical, reckoned on the chlorobenzene introduced.
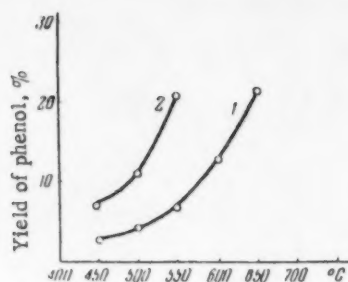
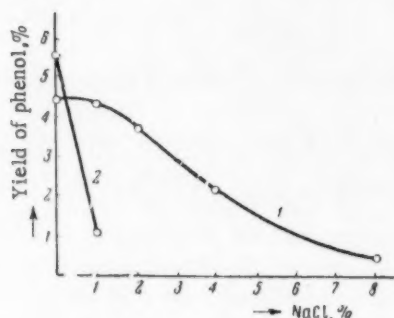Fig. 1. Catalytic activity of (1) phosphate, (2) silica gel.

Fig. 2. Deactivation of phosphate (1) and silica gel (2) catalysts by sodium chloride in the hydrolysis of chlorobenzene at 500°.
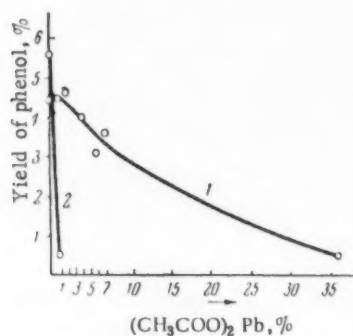

Fig. 3. Deactivation of phosphate (1) and silica gel (2) catalysts by lead acetate in the hydrolysis of chlorobenzene at 500°.

Preliminary experiments established that metaphosphoric acid, copper phosphate and dicalcium phosphate are inactive in this reaction. Commercial grades of tricalcium phosphate (Russian and Kahlbaum) evidently contain impurities; these, too, had poor activity and were unstable. Unlike them, the tricalcium phosphate that we prepared from soluble calcium salts and phosphoric acid or by neutralization of calcium hydroxide with acid had high activity and stability. This is illustrated by Figs. 1-3 in which curves characterizing the activity of silica gel at various temperatures and its deactivating mineral impurities are compared with curves for phosphate on the basis of our previously published data.

It follows from Table 1 and Fig. 1 that in presence of phosphate catalyst the vapor-phase hydrolysis of chlorobenzene takes place with measurable velocity in the same temperature range as with silica gel (450-600°). The activity of phosphate catalyst is lower than that of silica gel. In order to obtain the same yield of phenol as on silica gel, it is necessary to raise the reaction temperature by approximately 100°. Using freshly prepared phosphate catalyst at 450°, the yield of hydrochloric acid is seen to be lower than that of phenol. In the subsequent experiments at 500 and 550°, with a longer duration, the yields of acid and phenol are equal. With phosphate catalyst the reaction goes with a high degree of selectivity up to 550°. At higher temperatures the yield of hydrochloric acid sharply exceeds the phenol yield (evidence of secondary reactions). The results of our experiments confirm that the phosphate catalyst itself (in the absence of promoters) is active in the investigated reaction.

Table 2 contains the data for the influence of calcination on the activity of phosphate catalyst. We see that the yield of phenol in the experiment at 500° (carried out over the catalyst after an experiment at 650° followed by regeneration for 2 hrs) was nearly the same (4%) as before the experiment at 650° (4.4%). Similar data were obtained in the last two experiments (Table 1) at 500° which were likewise performed after experiments at 650°. It follows from the other experiments of Table 2 that over a catalyst calcined for 2 hrs in air at 850°, the phenol yield in the 500° experiment is 0.9%, and in the 550° experiment 2.2%.

The catalyst accordingly nearly fully retained its activity after the 650° experiment followed by regeneration. Only after calcination at 850° did the catalytic activity of the phosphate fall by a factor of 4 to 5. Comparison of these results with previous ones shows that the thermal stability of phosphate catalyst is higher than that of silica gel [11].

We established earlier that inorganic impurities such as NaCl and lead acetate, added in the proportion of 1%, nearly completely deactivate a silica gel catalyst [12]. The phosphate catalyst behaves differently. Tables 3

TABLE 1

Hydrolysis of Chlorobenzene in Presence of Phosphate Catalyst *

$H_2O:C_6H_5Cl$ Ratio	Temperature in °C	Yield in %	
		C_6H_5OH	HCl
1.1	450	4.2	—
0.9	450	3.3	0.2
1.1	450	2.2	0.5
1.1	500	5.6	0.9
1.0	500	5.4	2.1
1.1	500	3.7	2.8
1.0	500	3.2	2.5
1.1	550	8.1	6.4
1.2	550	6.9	6.8
0.8	550	5.4	6.2
0.8	600	12.5	14.6
1.1	600	12.4	15.6
1.2	650	21.4	28.0
0.9	650	9.6 **	16.7
1.0	500	3.8	3.7
0.8	500	4.3	4.4

* The catalyst was regenerated by treatment with air for 2-4 hrs at 525-550° on transition to each fresh temperature.

** The sharp drop in activity of the catalyst in this experiment is evidently due to surface contamination.

TABLE 2

Thermal Stability of Phosphate Catalyst

Nature of thermal treatment	Exptl. temp. in °C	Yield in %	
		C_6H_5OH	HCl
Before 650° expt.	500	4.4	2.1
After 650° expt.	500	4.0	4.0
After calcination at 850°	500	0.9	0.8
Before calcination at 850°	550	7.2	—
After calcination at 850°	550	2.2	—

TABLE 3

Deactivation of Phosphate Catalyst by Sodium Chloride

Wt.% of sodium chloride in catalyst	Exptl. temperature, °C	Yield in %	
		C_6H_5OH	HCl
0.0	500	4.5	2.1
1.0	500	4.4	3.0
2.0	500	3.8	3.5
4.0	500	2.2	—
8.0	500	0.5	1.8

TABLE 4

Deactivation of Phosphate Catalyst by Lead Acetate

Wt.% of lead acetate in catalyst	Temperature, °C	Yield in %	
		C_6H_5OH	HCl
0.0	500	4.5	2.1
1.0	500	4.5	4.7
2.0	500	4.6	5.0
4.0	500	4.0	4.7
6.0	500	3.1	3.1
7.0	500	3.6	4.0
36.0	500	0.4	0.8

and 4 and Figs. 2 and 3 contain data for the phenol yield when working with specimens of phosphate catalyst impregnated with various amounts of sodium chloride and lead acetate. These data show that phosphate is nearly unaffected by addition of 1-2% of inorganic impurity.
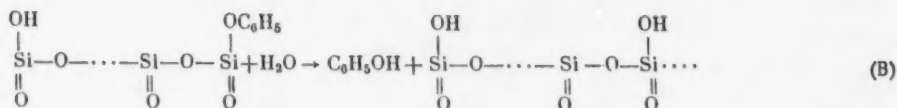
A considerable deactivation of the phosphate is only observed after addition of 8% of sodium chloride; even more lead acetate is required to produce a similar effect.

Mechanism of the activating action of calcium phosphate. Our investigation of the mechanism of the vapor-phase hydrolysis of aryl chlorides led us to the conclusion that the catalytic action of silica gel is

governed by its free OH groups [5]. The labile hydrogen atom in the OH group of silica gel reacts with chlorobenzene at the C—Cl bond:

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{Si}-\text{O}-\cdots-\text{Si}-\text{O}-\text{Si} \\
\| \\
\text{O}
\end{array}
+ C_6H_5Cl \rightarrow
\begin{array}{c}
\text{OC}_6\text{H}_5 \\
| \\
\text{Si}-\text{O}-\cdots-\text{Si}-\text{O}-\text{Si} \\
\| \\
\text{O}
\end{array}
+ HCl \cdots \qquad (A)
$$
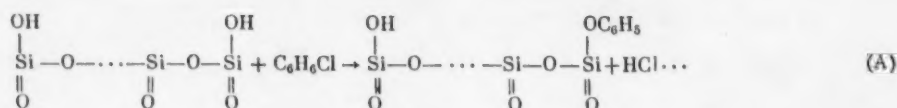
The ester group formed intermediately on the surface of the silica gel is subsequently hydrolyzed noncatalytically:

$$
\begin{array}{c}
\text{OC}_6\text{H}_5 \\
| \\
\text{Si}-\text{O}-\cdots-\text{Si}-\text{O}-\text{Si} \\
\| \\
\text{O}
\end{array}
+ H_2O \rightarrow C_6H_5OH +
\begin{array}{c}
\text{OH} \\
| \\
\text{Si}-\text{O}-\cdots-\text{Si}-\text{O}-\text{Si} \\
\| \\
\text{O}
\end{array}
\cdots \qquad (B)
$$

Phenol is formed in stage B and the OH groups of silica gel are regenerated and can catalyze the reaction over and over again.

We suggest that our proposed mechanism of the catalysis of the vapor-phase hydrolysis of an aromatically combined halogen by silica gel is also applicable to calcium phosphate crystal hydrate. As was shown in Semishin's investigations, solid crystal hydrates (metallic salts) are compounds with more or less pronounced acidic properties which differ only qualitatively from solid acids and acid salts [13]. At 400-500° the lability of hydrogen in crystal hydrates must be still greater. This fact justifies our assumption that the catalytic activity of tricalcium phosphate is likewise associated with its OH groups which contain a labile hydrogen atom:
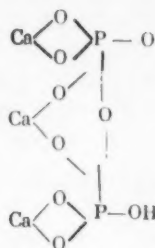
From this aspect, the high thermal stability of the catalyst can be attributed to the high stability of the crystal hydrate of tricalcium phosphate at high temperature.

SUMMARY

1. The vapor-phase hydrolysis of chlorobenzene in presence of phosphate catalysts was investigated. The activity of a one-component phosphate catalyst in the absence of promoters was confirmed.

2. The influence of the temperature on the degree of conversion of chlorobenzene and on the selectivity of the reaction was investigated. It was found that the phosphate catalyst has a higher thermal stability than silica gel and is less sensitive to the deactivating action of inorganic impurities.

3. It is suggested that the mechanisms of vapor-phase hydrolysis are the same in presence of phosphate and silica gel catalysts.

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THE TELOMERIZATION REACTION AND THE CHEMICAL TRANSFORMATIONS
OF TELOMERS

R. Kh. Freidlina

Report to the Session of the Division of Chemical Sciences of the Academy of Sciences, USSR

on October 30, 1957

Telomerization and chemical transformations of telomers were selected as the theme of synthetic studies in recent years by a group at the heteroorganic synthesis laboratory of the Institute of Heteroorganic Compounds of the Academy of Sciences USSR. Up to the present time the compounds most accessible by synthesis of aliphatic compounds have been low-molecular substances containing 1-6 carbon atoms and high-molecular compounds containing many thousands of atoms in the molecule. Between these two extremes is the region of compounds of "medium" molecular weight which has been little investigated.
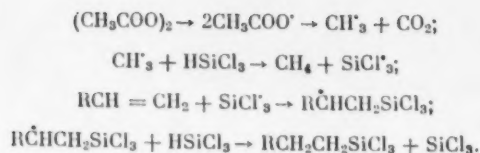
We consider that the telomerization reaction, being a controlled polymerization reaction, will afford the possibility of penetrating into this neglected region. Telomerization is further attractive in that it opens up the possibility of easily constructing molecules containig specific terminal groups because these groups depend upon the character of the starting substance (chain-transfer reaction). Finally, by providing a series of individual telomer-homologs, the reaction offers the possibility of easily obtaining a series of identically constructed substances differing in respect to the length of the segment linking the reactive groups. This last possibility is important for the study of a number of general problems such as the mutual influence of groups in a molecule.
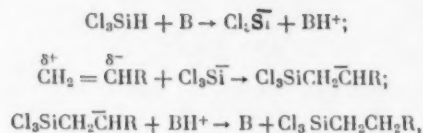
The Telomerization Reaction

We made a particularly detailed study of the already well-known reactions of telomerization of ethylene with carbon tetrachloride [1] and chloroform [2]. Results of these investigations were reported in a series of publications [3-5]. Here we merely note that we succeeded in showing that, contrary to what is stated in the literature, higher $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and $\alpha,\alpha,\alpha,$-trichloroalkanes can be obtained at relatively low pressures (100-200 atmos). The main factor governing the medium molecular weight of the telomers is the ethylene/carbon tetrachloride and ethylene/chloroform molar ratio employed in the reaction zone.

We succeeded in isolating in the pure form the previously unknown $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes containing 11 to 23 carbon atoms in the molecule; also narrow fractions of tetrachloroalkanes with an average content of 25, 35 and 51 atoms of carbon [4, 6]. In the case of α,α,α-trichloroalkanes we isolated previously unknown compounds containing 13-17 carbon atoms [4]. In joint work with the Institute of the Nitrogen Industry (Ovakimyan and Beer) we organized the experimental production of lower $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes [3, 7], and jointly with the Institute for Synthetic and Natural Perfumes (Belov), we organized the experimental production of higher tetrachloroalkanes [5]. Recently we developed a new reaction — thermal telomerization of olefins with silanes containing the Si—H bond [8, 9]. The choice of silanes as reaction chain carriers was prompted by the importance of organosilicon compounds in industry; in this connection the application of the telomerization reaction was extremely attractive.

Compounds of silicon containing the Si—H bond are capable of adding on at the double and triple bond of unsaturated compounds. Reactions of this type can be effected by several slightly differing mechanisms. For additions of silanes to olefins, for example, initiated by ultraviolet irradiation or by addition of peroxides or azo compounds, the following radical chain mechanism is advanced [10]:

$$(CH_3COO)_2 \rightarrow 2CH_3COO^{\cdot} \rightarrow CH^{\cdot}_3 + CO_2;$$

$$CH^{\cdot}_3 + HSiCl_3 \rightarrow CH_4 + SiCl^{\cdot}_3;$$

$$RCH = CH_2 + SiCl^{\cdot}_3 \rightarrow R\overset{\cdot}{C}HCH_2SiCl_3;$$

$$R\overset{\cdot}{C}HCH_2SiCl_3 + HSiCl_3 \rightarrow RCH_2CH_2SiCl_3 + SiCl_3.$$

An ionic mechanism is proposed on the other hand for addition reactions taking place in presence of bases [11, 12]:

$$Cl_3SiH + B \rightarrow Cl_3\overline{Si} + BH^+;$$

$$\overset{\delta^+}{CH_2} = \overset{\delta^-}{CHR} + Cl_3\overline{Si} \rightarrow Cl_3SiCH_2\overline{C}HR;$$

$$Cl_3SiCH_2\overline{C}HR + BH^+ \rightarrow B + Cl_3 SiCH_2CH_2R,$$

where B is an organic base, R = CN, CH$_2$CN.

In the case of thermal addition of trichlorosilane to olefins at a temperature of 160-400°, the existence of a transition state was postulated; in this state the electron-accepting silicon atom joins onto the methylene group of the olefin R—CH=CH$_2$, while the chlorine atom links up with the neighboring carbon atom; thereupon the exchange of the latter with the labile hydrogen atom of the silane gives the end product [13]. Work has also been described on the addition of silanes to olefins and acetylene in presence of catalysts (group VII metals such as platinum on carbon, platinized asbestos, platinum black [14, 15] and palladium on various supports [16]; likewise chloroplatinic acid, iridium chloride and ruthenium chloride [17]). The addition of trichlorosilane to acrylonitrile in presence of Raney nickel [18] and of tetrapyridinenickel chloride [11] has also been described; in the second case a mixture of two isomeric addition products was obtained. The mechanism of the reactions in presence of catalysts has not been investigated.

It seemed that the free radical-initiated radical chain addition reaction should be easily transformed into a telomerization reaction under conditions affording an excess of olefin and a sufficiently high concentration of olefin in the reaction mixture. On the other hand, the thermal reaction, even if it possesses the chain mechanism attributed to it, could not pass over into a telomerization reaction as a result merely of alteration of the relative concentration of starting compounds. A paper published in 1956 described an example of a telomerization reaction in this field. Reaction of perfluoroethylene with trichlorosilane, initiated by ultraviolet irradiation, gave
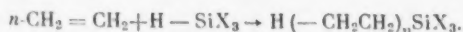
TABLE 1

Thermal Telomerization of Silanes with Olefins

Expt. No.	Olefin	Silane	Temperature in °C	Pressure, atmos	Duration in hrs	Structure of products obtained	n^*
1	CH$_2$=CH$_2$	H — SiCl$_3$	285	200	2	H (CH$_2$CH$_2$) nSiCl$_3$	1—5
2	CH$_2$=CH$_2$	H — SiCl$_2$CH$_3$	260—270	560	2	H (CH$_2$CH$_2$) nSiCl$_2$CH$_3$	1—6
3	CH$_2$=CH$_2$	H — SiCl$_2$C$_6$H$_5$	280—300	90	3	H (CH$_2$CH$_2$) nSiCl$_2$C$_6$H$_5$	1—3
4	CH$_2$=CH$_2$	H — Si (C$_2$H$_5$)$_3$	300—310	200	4	H (CH$_2$CH$_2$)nSi (C$_2$H$_5$)$_3$	1—2
5	CH$_3$CH=CH$_2$	H — SiCl$_2$CH$_3$	260—275	100	3	H (C$_3$H$_6$) nSiCl$_2$CH$_3$	1—3

* The value of $\underline{n}$ relates to substances isolated from the reaction mixture in the pure form.

compounds of the structure H(—CF$_2$CF$_2$)nSiCl$_3$, where n = 1, 2, 3 [19]. An attempt at thermal realization of this reaction gave perfluorocyclobutane and small quantities of organosilicon compounds which could not be isolated in pure forms. It must be remembered that perfluoroethylene polymerizes with very great facility and differs from olefins in entering into a telomerization reaction even with hydrocarbons.

Our attempts to effect a telomerization reaction in stainless steel autoclaves, starting from methyldichlorosilane, ethyldichlorosilane, triethylsilane and ethylene or propylene in presence of benzoyl peroxide, tert.-butyl peroxide or azodiisobutyronitrile were unsuccessful. These experiments were carried out at 100-140° and 100-300 atmos.* We demonstrated the occurrence of a telomerization reaction in reactions of ethylene with trichlorosilane, methyldichlorosilane, and phenyldichlorosilane, also of propylene with methyldichlorosilane, in stainless steel autoclaves at 250-300° and 100-500 atmos without addition of any initiators or catalysts. This telomerization reaction is represented by the equation:

$$n\text{-}CH_2 = CH_2 + H - SiX_3 \rightarrow H (- CH_2CH_2)_n SiX_3.$$

Some data characterizing these reactions are presented in Table 1.

The reaction conditions specified in Table 1 are not optimum. Telomerization of ethylene with methyldichlorosilane was studied in most detail. It was established that at 325-350° the conversion of methyldichlorosilane reaches 60-75% after only 5-10 min. Reaction at only 100 atmos using an ethylene/methyldichlorosilane molar ratio of 2:1 at about 285° gives higher telomers (n > 3 = 23% of the total products of the reaction). It is interesting to note that reaction between methyldichlorosilane and ethylene at 50-70 atmos (in an autoclave) in presence of a small quantity of chloroplatinic acid commences even at room temperature and proceeds with heat liberation and high velocity. A single reaction product is then obtained — methylethyldichlorosilane. The film of platinum formed on the autoclave walls is sufficient for repeated additional experiments without addition of fresh portions of platinum.

Great interest is attached to a study of the mechanism of thermal telomerization of olefins with silanes. If this reaction proceeds by way of homolytic dissociation of silanes at the Si—H bond, we should expect silanes of this type to be capable of functioning as initiators of radical processes at high temperature. Thermal telomerization is undoubtedly the simplest and most convenient method of preparation of dialkyldichlorosilanes of the type of $RSiCl_2(C_nH_{2n+1})$, previously not easily accessible, as well as of alkyltrichlorosilanes containing higher alkyls. The starting alkyldichlorosilanes are readily accessible substances; they are formed by direct synthesis from alkyl halides and silicon-copper alloys [20].
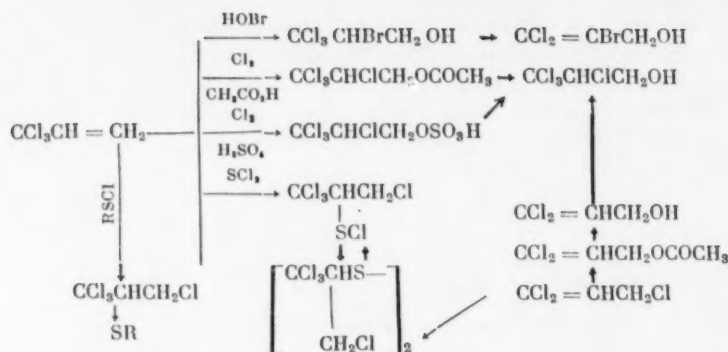
Chemical Transformations of $\alpha,\alpha,\alpha,\omega$-Tetrachloroalkanes

The chloromethyl and trichloromethyl groups in $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, separated by an inert polymethylene segment, behave independently in chemical reactions. An exception is 1, 1,1,3-tetrachloropropane in which the reciprocal effect of these groups is clearly manifested [6]. The properties of the trichloromethyl group have been scarcely studied in the past; conflicting data have even been published about the nature of its orientating effect.

Orientating properties of the trichloromethyl group. Reactions of electrophilic addition of hypobromous acid or chlorine in presence of sulfuric or acetic acid, sulfur dichloride, and phenylsulfenyl chloride to 1,1,1-trichloropropene in all cases went contrary to the Markovnikov rule, thereby demonstrating the electron-accepting character of the trichloromethyl group. These reactions and methods of confirming the structure of the addition compounds obtained (I, II, III, IV and V) are represented in Scheme 1.

Measurement of the dissociation constants of the acids $CCl_3(GH_2)_nCO_2H$ and of the basicity of trichloroalkylamines $CCl_3(CH_2)_nNH_2$ showed that the dissociation constants of the acids are higher than those of carboxylic and ω-chlorocarboxylic acids with the same number of atoms of carbon, while the basicity of the trichloroalkylamines is lower than that of the corresponding alkylamines with the same number of carbon atoms. The rapid damping of the effect of introduction of the trichloromethyl group with increasing number of methylene groups in the molecule indicates the inductive character of the influence of the CCl_3 group (Tables 2 and 3).

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* It should be noted that all previously described additions of silanes to olefins in presence of peroxides were realized in glass apparatus. An influence of the walls of the autoclave on the sequence of addition and on the yield of reaction products was observed when carrying out reactions of addition of trichlorosilane to, for example, acrylonitrile in presence of bases in autoclaves [11]. It was subsequently reported that metals affect the addition reaction of trichlorosilane with 1-pentene in presence of peroxides. Iron in particular functions as an inhibitor, while tin exerts a promoting effect in this reaction [17].

$$\begin{array}{l}
\xrightarrow{\text{HOBr}} CCl_3CHBrCH_2OH \;\rightarrow\; CCl_2=CBrCH_2OH \\[4pt]
\xrightarrow[\text{CH}_3\text{CO}_2\text{H}]{\text{Cl}_2} CCl_3CHClCH_2OCOCH_3 \;\rightarrow\; CCl_3CHClCH_2OH \\[4pt]
\xrightarrow[\text{H}_2\text{SO}_4]{\text{Cl}_2} CCl_3CHClCH_2OSO_3H \\[4pt]
\xrightarrow{\text{SCl}_2} CCl_3CHCH_2Cl
\end{array}$$

$$CCl_3CH=CH_2$$

$$\xrightarrow{\text{RSCl}} \;\; CCl_3CHCH_2Cl \;\big|\; SR$$

$$CCl_3CHCH_2Cl \quad\big|\quad SCl \;\rightarrow\; \big[\,CCl_3CHS\!-\!CH_2Cl\,\big]_2$$

$$CCl_2=CHCH_2OH$$
$$CCl_2=CHCH_2OCOCH_3$$
$$CCl_2=CHCH_2Cl$$

Scheme 1*

TABLE 2

Dissociation Constants of Aqueous Solutions of Acids [6]

Formula of acid	Dissociation constant	Temperature, °C
$CCl_3(CH_2)_2CO_2H$	$6.2 \cdot 10^{-5}$	20
$CH_3(CH_2)_2CO_2H$	$1.53 \cdot 10^{-5}$	18
$Cl(CH_2)_2CO_2H$	$3.0 \cdot 10^{-5}$	25
$CF_3(CH_2)_2CO_2H$	$6.98 \cdot 10^{-5}$	25
$CCl_3(CH_2)_3CO_2H$	$3.0 \cdot 10^{-5}$	20
$CH_3(CH_2)_3CO_2H$	$1.51 \cdot 10^{-5}$	18
$Cl(CH_2)_3CO_2H$	$2.04 \cdot 10^{-5}$	25
$CF_3(CH_2)_3CO_2H$	$3.2 \cdot 10^{-5}$	25

TABLE 3

Dissociation Constants of $CCl_3(CH_2)_nNH_2$ in Water at 20°

Formula	Dissociation constant
$CCl_3CH_2NH_2$	$2.0 \cdot 10^{-9}$
$CCl_3(CH_2)_2NH_2$	$3.0 \cdot 10^{-5}$
$CCl_3(CH_2)_3NH_2$	$6.0 \cdot 10^{-5}$
$CCl_3(CH_2)_4NH_2$	$9.0 \cdot 10^{-5}$
$CH_3CH_2NH_2$	$3.4 \cdot 10^{-4}$ (25°)
$CH_3(CH_2)_2NH_2$	$4.7 \cdot 10^{-4}$ (25°)
$CH_3(CH_2)_3NH_2$	$4.1 \cdot 10^{-4}$ (25°)

1,1,1-Trichloro-2-methylpropene adds on chlorine in presence of acetic acid and mercuric acetate, likewise contrary to the Markovnikov rule, with formation of 1,1,1,2-tetrachloro-2-methyl-3-acetoxypropane:

$$\begin{array}{c} CCl_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!C=CH_2 + Cl_2 \xrightarrow[\text{Hg(OCOCH}_3)_2]{\text{CH}_3\text{CO}_2\text{H}} \begin{array}{c} CCl_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!CClCH_2OCOCH_3.$$
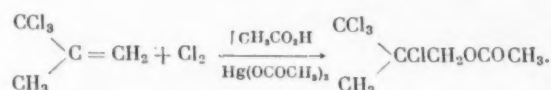
This fact points to the orientating effect of the CCl_3 group being more intense than the action of the methyl group.

Reaction of γ,γ,γ-trichlorocrotonic acid with benzene in presence of aluminum trichloride led to formation of α-phenyl-γ,γ-dichlorovinylacetic acid:

$$CCl_3CH=CH-CO_2H \xrightarrow[\text{AlCl}_3]{\text{C}_6\text{H}_6} CCl_2=CH-\underset{\underset{C_6H_5}{|}}{C}HCO_2H \rightarrow CH_3CH_2\underset{\underset{C_6H_5}{|}}{C}HCO_2H.$$
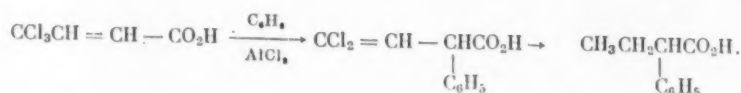
This fact can likewise be taken as evidence of the greater orientating effect of the CCl_3 group in comparison with the carboxyl group. These reactions undoubtedly demonstrate the character of the trichloromethyl group as a strong negative substituent.

* Reactions with dense arrows were used for verification of the structure of the addition compounds.

<u>Characteristic reactions of the trichloromethyl group.</u> The trichloromethyl group was found to be inert to the action of nucleophilic reactants [6]. We made extensive use of this property in synthetic reactions in which nucleophilic substitution of the chlorine in the chloromethyl group was effected while the CCl_3 group was maintained intact. Electrophilic and radical agents act on the trichloromethyl group. Thus, concentrated sulfuric acid and anhydrous nitric acid hydrolyze the CCl_3 group to carboxyl. Hydrolysis of the CCl_3 group by sulfuric acid was already well-known; our discovery of the reaction with nitric acid reveals a new method of transition from tetrachloroalkanes to carboxylic acids [21]. This is the only method to give good yields in the case of higher tetrachloroalkanes. Metallic halides of the type of Friedel-Crafts catalysts cause dehydrochlorination of tetrachloroalkanes with loss of chlorine from the trichloromethyl group. We developed a simple and convenient means of transition from tetrachloroalkanes to trichloroalkenes by catalytic dehydrochlorination by the action of $AlCl_3$, $FeCl_3$ or $SbCl_5$ under mild conditions in the absence of solvents [6].

The accessibility of trichloroalkenes of the structure $Cl(CH_2)_nCH{=}CCl_2$ has opened up extensive possibilities of synthesis on their basis. In pa~~icular, we devised a method of transformation of compounds containing the di-chlorovinyl group into α-chlorocarboxylic acids by conjugated addition of chlorine in a medium of concentrated sulfuric acid or anhydrous formic acid [22]. Under the action of radical reactants such as nickel, as well as hydrogen, in presence of Raney nickel, chlorine splits off from the CCl_3 group and the residue dimerizes with formation of hexachloroalkanes with the structure $[Cl(CH_2)_n CCl_{2-}]_2$, containing twice as many carbon atoms as the starting tetrachloroalkane [6]. Taking the above-discussed characteristics of the trichloromethyl group into consideration, we synthesized about seven hundred compounds, starting from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes. The methods of preparation of these compounds cannot be systematically considered within the framework of the present report. We limit ourselves here to a few examples of syntheses.
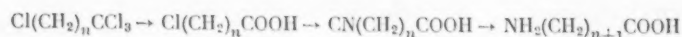
Aminocarboxylic Acids

<u>ω-Aminocarboxylic acids containing an odd number of carbon atoms.</u> These are obtained with extreme simplicity from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes in two steps:
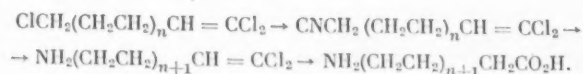
$$Cl(CH_2)_n CCl_3 \rightarrow Cl(CH_2)_n CO_2H \rightarrow NH_2(CH_2)_n CO_2H.$$
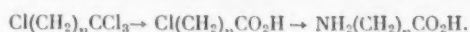
This route is the basis of the industrial synthesis of ω-aminoenanthic and ω-aminopelargonic acids that we developed in association with the State Institute of the Nitrogen Industry and carried out on the semitechnical scale [3, 23]. In association with Strepikheev, Topchibasheva and Shein [23, 24], the All-Union Institute of Research on Synthetic Fibers developed methods of polycondensation of these acids and obtained new polyamide fibers named "enant" and "pelargon." These new fibers possess a number of advantages over other polyamide fibers both from the technological aspect of manufacture of the resins and fibers and from the standpoint of their properties.
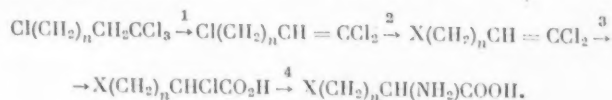
<u>ω-Aminocarboxylic acids containing an even number of carbon atoms.</u> We prepared these according to the scheme:

$$Cl(CH_2)_n CCl_3 \rightarrow Cl(CH_2)_n COOH \rightarrow CN(CH_2)_n COOH \rightarrow NH_2(CH_2)_{n+1}COOH$$

An alternative scheme is:

$$ClCH_2(CH_2CH_2)_n CH = CCl_2 \rightarrow CNCH_2(CH_2CH_2)_n CH = CCl_2 \rightarrow$$
$$\rightarrow NH_2(CH_2CH_2)_{n+1}CH = CCl_2 \rightarrow NH_2(CH_2CH_2)_{n+1}CH_2CO_2H.$$
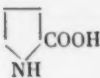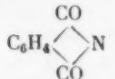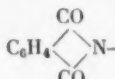
By these routes we synthesized ω-aminocarboxylic acids containing 7 to 11 carbon atoms. We also synthesized a series of α-amino acids including natural amino acids, their homologs and derivatives: proline, ornithine, lysine, glutamic acid, α-aminoadipic acid, α-aminopimelic acid, α-aminosuberic acid, phenylalanine, and p-chlorophenylalanine according to Scheme 2:

$$Cl(CH_2)_n CH_2CCl_3 \xrightarrow{1} Cl(CH_2)_n CH = CCl_2 \xrightarrow{2} X(CH_2)_n CH = CCl_2 \xrightarrow{3}$$
$$\rightarrow X(CH_2)_n CHClCO_2H \xrightarrow{4} X(CH_2)_n CH(NH_2)COOH.$$

Scheme 2

TABLE 4

Methods of Preparation of Compounds $X(CH_2)_nCH{=}CCl_2$ for Later Synthesis of Amino Acids

Starting trichloroalkene	$X(CH_2)_n CH{=}CCl_2$		Structure of amino acids prepared by Scheme 2
	X	Method of introduction of X	
$Cl(CH_2)_3 CH{=}CCl_2$	Cl		
$Cl(CH_2)_3 CH{=}CCl_2$	$C_6H_4 \overset{CO}{\underset{CO}{\diamondsuit}} N$	Potassium phthalimide	$NH_2(CH_2)_3CH(NH_2)CO_2H$
$Cl(CH_2)_3 CH{=}CCl_2$	$C_6H_4 \overset{CO}{\underset{CO}{\diamondsuit}} N{-}CH_2$	Intro. of CN—, reduction with lithium aluminum hydride, potassium phthalimide	$NH_2(CH_2)_4 CH(NH_2)CO_2H$
$Cl(CH_2)_3 CH{=}CCl_2$	COOH	Intro. of CN—, hydrolysis	$HOOC(CH_2)_3 CH(NH_2)CO_2H$
$Cl(CH_2)_3 CH{=}CCl_2$	CH_2COOH	Malonic synthesis	$HOOC(CH_2)_4 CH(NH_2)CO_2H$
$Cl(CH_2)_5 CH{=}CCl_2$	COOH	Intro. of CN—, hydrolysis	$HOOC(CH_2)_5 CH(NH_2)CO_2H$
$ClCH_2CH{=}CCl_2$	CH_2COOH	Malonic synthesis	$HOOC(CH_2)_2CH(NH_2)CO_2H$
$ClCH_2CH{=}CCl_2$	C_6H_5	Friedel-Crafts condensation with benzene	$C_6H_5CH_2CH(NH_2)CO_2H$
$ClCH_2CH{=}CCl_2$	ClC_6H_4	Condensation with chlorobenzene	$ClC_6H_4CH_2CH(NH_2)CO_2H$

The first step of this reaction (preparation of α,α,ω-trichloroalkenes by catalytic dehydrochlorination of tetrachloroalkanes) is effected with nearly quantitative yield. Methods of preparation of $X(CH_2)_nCH{=}CCl_2$ from trichloroalkenes used in the synthesis of the amino acids enumerated above are listed in Table 4. In most cases we were able to find reaction conditions that ensured good yields.

Transformation of dichlorovinyl compounds into the corresponding α-chlorocarboxylic acids (step 3 of Scheme 2) became possible thanks to our previously developed method of conjugated addition of chlorine to the dichlorovinyl group in a medium of concentrated sulfuric acid. The mild conditions of this reaction enable it to be extensively applied to dichlorovinyl compounds containing diverse substituents such as COOH, CCl_3, NH_2 and C_6H_4Cl. When this reaction is carried out, however, with 1,1–dichloro-3-phenylpropene-1 instead of α-chloro-β-phenylpropionic acid, more highly chlorinated compounds are formed. We succeeded in preparing α-chloro-β-phenylpropionic acid by addition of chlorine to phenyldichloropropene in a medium of anhydrous formic acid. Ammonolysis of the resultant chloroacids (step 4 of Scheme 2) leads to the corresponding α-amino acids.

The proposed route for synthesis of α-amino acids has the advantages of accessibility of the starting substances, simplicity of preparation of many of the intermediates enumerated (especially trichloroalkenes), facility of transition from the synthesis of one amino acid to the synthesis of another by using in many cases the same starting and intermediate compounds. The method gives amino acids free of foreign amino acids.

The foregoing examples by no means exhaust the possibilities of synthesis of ω- and α-amino acids. It suffices to recall, for example, that $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes of normal structure may be replaced in these syntheses by many other compounds containing the trichloromethyl group, such as compounds obtained by addition to olefins of carbon tetrachloride, bromotrichloromethane and chloroform; likewise by telomerization of diverse olefins with carbon tetrachloride.
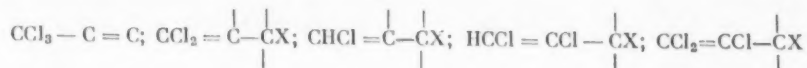
Sulfur-Containing Compounds

ω-Substituted sulfur-containing compounds were obtained by replacement of the chlorine in the chloromethyl group of tetrachloroalkanes by a functional group containing sulfur [25]. α-Substituted compounds of this type were obtained by addition of sulfur chloride or polychloride at the double bond of dichlorovinyl compounds in a neutral or acidic medium. δ,δ'-Thiodivaleric acid was synthesized on the experimental scale. According to the data of the Plastic Masses Research Institute (Moshkin), esters of thiodivaleric acid are good plasticizers for polyvinyl chloride and can replace esters of acids obtained from edible raw materials. In recent joint work by INEOC and VNIIV (Korshak, Chelnokova and Shein) a new sulfur-containing polyamide fiber was obtained on the basis of a salt of thiodivaleric acid and hexamethylenediamine; the structure of the elementary unit of this high-molecular compound may be represented by the formul $[-NH-CO(CH_2)_4S(CH_2)_4-CONH(CH_2)_6-]$. The first specimens of this unusual fiber are comparable to capron in strength and elongation.

Dicarboxylic Acids

Starting from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, diverse dicarboxylic acids can be obtained by many routes: we may single out for special mention ω,ω'-dicarboxylic acids of normal structure containing 6, 7, 8, 9, 10, 12 and 14 carbon atoms; α-amino-substituted ω,ω'-dicarboxylic acids with 5, 6, 7 and 8 carbon atoms; dicarboxylic acids containing an aromatic ring of the type of p-$HOOC(CH_2)_nC_6H_4(CH_2)_nCOOH$; dicarboxylic acids of the type of A $[(CH_2)_n CO_2H]_2$, where A = S, SO, SO$_2$, S$-$S, NH, NR.

Dicarboxylic acids of normal structure with an even number of carbon atoms were prepared from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes by introduction of a nitrile group and subsequent hydrolysis of both terminal groups (nitrile and trichloromethyl); the reverse sequence is sometimes possible (hydrolysis of the trichloromethyl group followed by introduction and hydrolysis of the nitrile group).

For synthesis of dicarboxylic acids containing an odd number of carbon atoms, tetrachloroalkanes are saponified to ω-hydroxycarboxylic acids, and oxidation of the latter (say with nitric acid) gives dicarboxylic acids with the same number of carbon atoms as in the corresponding starting tetrachloroalkanes. Dicarboxylic acids containing an aromatic ring were obtained by Friedel-Crafts condensation of benzene with ω-chlorocarboxylic acids. In collaboration with the All-Union Institute of Perfume Research we started the experimental production of ω-hydroxypelargonic acid, azelaic acid and other higher hydroxy acids. In the course of this investigation we carried out many interesting laboratory studies on general problems of organic chemistry. In particular we may mention the work with Zakharkin on the allylic anionotropic rearrangement in the systems.

$$CCl_3-C=C;\; CCl_2=\overset{|}{C}-\overset{|}{C}X;\; CHCl=\overset{|}{C}-\overset{|}{C}X;\; HCCl=CCl-\overset{|}{C}X;\; CCl_2=CCl-\overset{|}{C}X$$

and on the allylic prototropic rearrangement [6] in systems

$$CCl_2=C\,\overset{|}{C}HCO_2R;\; CCl_2=\overset{|}{C}-\overset{|}{C}HCN;$$
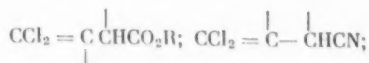
We also studied the chemical properties characterizing such groups as CCl_3, CCl_3CHCl, $CCl_3C=C$, $CCl_2=CH$, $CCl_2=CH-\overset{|}{C}X$ [6] . Here we shall limit ourselves to a brief discussion of only one study devoted to homolytic isomerization in the polyhalopropene series.
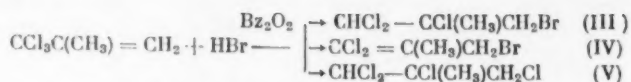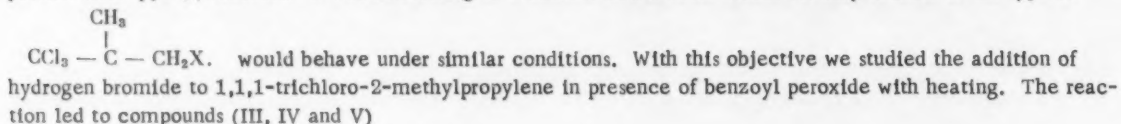
Homolytic Rearrangement in the Polyhalopropene Series

The study of rearrangements in organic radicals in solutions is a new field of investigation. This problem has not yet been considered in any of the published treatises on the chemistry of free radicals. The recent literature contains only one short survey in Japanese [26]. The very possibility of such an isomerization of alkyl radicals in solutions was disputed even recently [27]. In 1951 we showed in our laboratory [6] that addition of hydrogen bromide or of bromotrichloromethane to 1,1,1-trichloropropylene by heating in presence of benzoyl peroxide is accompanied by rearrangement of intermediately formed radicals of the type of (I) into radicals of the type of(II).

$$CCl_3\dot{C}H - CH_2X \rightarrow \dot{C}Cl_2CHClCH_2X,$$
$$(I) \qquad\qquad (II)$$
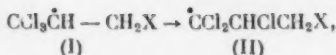
where X = CCl_3, Br, or Cl. Very recently we obtained new data in this field [2]. It was found that also addition of bromine to 1,1,1-trichloropropylene in nonpolar media in presence of benzoyl peroxide likewise results in re-arrangement under the action of heat or of irradiation; the products are 1,1,2-trichloro-1,3-dibromopropane and the normal product of addition (1,1,1-trichloro-2,3-dibromopropane). This observation is of fundamental interest because reaction with bromine is frequently employed for verification of structure, for identification, and for se-paration of unsaturated compounds.

This rearrangement of radicals is evidently associated with the greater stability of type (II) radicals in com-parison with type (I) radicals. It was interesting to elucidate how a more stable tertiary radical of the type of

$$CCl_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2X.$$ would behave under similar conditions. With this objective we studied the addition of hydrogen bromide to 1,1,1-trichloro-2-methylpropylene in presence of benzoyl peroxide with heating. The reac-tion led to compounds (III, IV and V)

$$CCl_3C(CH_3) = CH_2 + HBr \xrightarrow{Bz_2O_2} \begin{cases} \rightarrow CHCl_2 - CCl(CH_3)CH_2Br & (III) \\ \rightarrow CCl_2 = C(CH_3)CH_2Br & (IV) \\ \rightarrow CHCl_2 - CCl(CH_3)CH_2Cl & (V) \end{cases}$$

Formation of these compounds may be accounted for by a scheme involving rearrangement at steps d) and g)

a) $(C_6H_5COO) \rightarrow R^{\cdot}$;

b) $HBr - R^{\cdot} \rightarrow RH + Br$;

c) $CCl_3C(CH_3) = CH_2 + Br \rightarrow CCl_3\dot{C}(CH_3)CH_2Br$;

d) $CCl_3\dot{C}(CH_3)CH_2Br \xrightarrow{\text{rearrangement}} CCl_2C(CH_3)ClCH_2Br$;

e) $\dot{C}Cl_2C(CH_3)ClCH_2Br + HBr \rightarrow HCCl_2C(CH_3)ClCH_2Br + Br$;

f) $\quad\quad |+ CCl_3C(CH_3) = CH_2$
$\xrightarrow{\qquad\qquad} CCl_2 = C(CH_3)CH_2Br + CCl_3\dot{C}(CH_3)CH_2Cl$;
rearrangement

g) $CCl_3\dot{C}(CH_3)CH_2Cl \xrightarrow{\text{rearrangement}} \dot{C}Cl_2C(CH_3)ClCH_2Cl$;

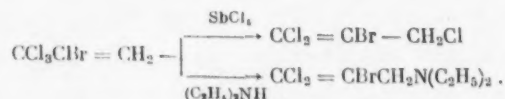h) $\dot{C}Cl_2C(CH_3)ClCH_2Cl + HBr \rightarrow HCCl_2C(CH_3)ClCH_2Cl + Br$.

All of these rearrangements took place in the course of addition reactions. Great interest is attached to a study of homolytic rearrangement of a given substance into an isomer. Only in the cases of a few of the isomeriza-tions described in the literature can there be any doubt as to whether the rearrangement is of a homolytic charac-ter. An example is the homolytic character, postulated by Hughes [29], of the tautomeric transformation of allyl bromides catalyzed by oxygen and hydrogen bromide; this has not yet, however, been experimentally confirmed. It should also be noted that the homolytic rearrangement of allyl bromides, which leads to the same products as anionotropic (heterolytic) rearrangement, is more difficult to investigate.

We established that 1,1,1-trichloro-2-bromopropylene isomerizes, after standing for a certain induction period, to 1,1,2-trichloro-3-bromopropylene-1:

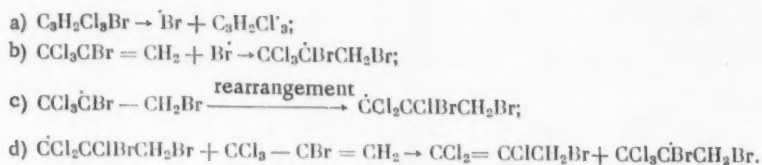$$CCl_3CBr = CH_2 \rightarrow CCl_2 = CClCH_2Br.$$
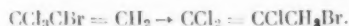
It is difficult to cite an analogy to the observed isomerization which involved translocation of the atoms of chlorine and bromine to neighboring carbon atoms and shifting of the double bond. The following data support the homolytic character of this isomerization. The reaction has an induction period (1-2 days) but under ultra-violet irradiation it commences quickly and proceeds quickly. Addition of dimethylaniline or hydroquinone in-hibits the reaction. Addition of azodiisobutyronitrile to 1,1,1-trichloro-2-bromopropylene in association with

gentle heating speeds up the isomerization in comparison with that of a pure specimen under identical conditions. It is also significant that the heterolytic isomerization of 1,1,1-trichloro-2-bromopropylene under the action of either electrophilic or nucleophilic agents takes the form of an allylic rearrangement:

$$CCl_3CBr = CH_2 - \begin{array}{c} \xrightarrow{\hspace{0.5cm} SbCl_5 \hspace{0.5cm}} CCl_2 = CBr - CH_2Cl \\ \xrightarrow[(C_2H_5)_2NH]{} CCl_2 = CBrCH_2N(C_2H_5)_2 . \end{array}$$

Under the action of antimony pentachloride, for example, 1,1,1-trichloro-2-bromopropylene rearranges to its allylic isomer 1,1,3-trichloro-2-bromopropylene-1.

Reaction of 1,1,1-trichloro-2-bromopropylene with diethylamine on heating gives the diethylamino derivative of the allylic isomer, 1,1-dichloro-2-bromo-3-diethylaminopropane. We postulate that the observed homolytic isomerization of 1,1,1-trichloro-2-bromopropylene to 1,1,2-trichloro-3-bromopropylene-1 goes according to the following scheme:

a) $C_3H_2Cl_3Br \rightarrow \dot{B}r + C_3H_2Cl_3$;

b) $CCl_3CBr = CH_2 + \dot{B}r \rightarrow CCl_3\dot{C}BrCH_2Br$;

c) $CCl_3\dot{C}Br - CH_2Br \xrightarrow{\text{rearrangement}} \dot{C}Cl_2CClBrCH_2Br$;

d) $\dot{C}Cl_2CClBrCH_2Br + CCl_3 - CBr = CH_2 \rightarrow CCl_2 = CClCH_2Br + CCl_3\dot{C}BrCH_2Br$.

Our studies of homolytic isomerization in polyhalopropylenes of the type of $CCl_3-CBr=CH_2$ are of great interest because the isomerization goes under mild conditions (at room temperature) with quantitative yield of the isomeric compound. The structure of the products of homolytic isomerization is not the same as that of products of heterolytic, allylic rearrangement. This work opens up new possibilities of research which can be expected to deepen our knowledge of the properties of radicals in solutions and to provide new possibilities of synthesis.

SUMMARY

1. The investigation revealed the great potentialities of telomerization in organic reactions.

2. Taking the telomerization of olefins with silanes as an example, the applicability of the telomerization reaction to the synthesis of heteroorganic compounds is demonstrated.

3. Investigation of hetero- and homolytic reaction of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes led to new routes for synthesis of diverse bi- and polyfunctional compounds.

4. Homolytic isomerization (not of the allylic type) was observed for the first time in the polyhalopropylene series.

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# ALLYLIC REARRANGEMENTS OF 1,1-DICHLORO-3-PHENYLPROPENE-1
AND RELATED COMPOUNDS

L. I. Zakharkin and V. V. Korneva

The allylic prototropic rearrangement in the dichloropropene system $>CH = \overset{|}{C} = CCl_2 \rightarrow \ > C = \overset{|}{C} - CHCl_2$ is known only in the case of γ,γ-dichlorovinylacetic acid and a series of its derivatives [1, 2]. In the present work we investigated the possibility of a similar rearrangement in the case of 1,1-dichloro-3-phenylpropene-1 and of some related compounds. Treatment of 1,1-dichloro-3-phenylpropene-1 (I) with sodium ethoxide in alcoholic solution causes an energetic reaction with formation of two compounds: cinnamaldehyde diethylacetal and phenyl vinyl ketone diethylketal:
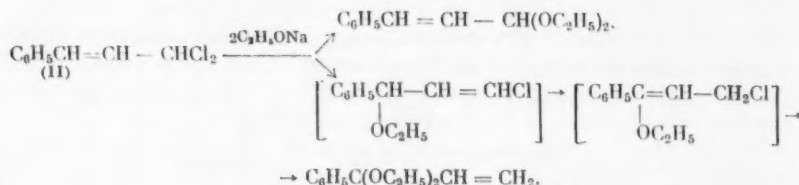
$$C_6H_5CH_2CH = CCl_2 + 2C_2H_5ONa \rightarrow C_6H_5CH = CH - CH(OC_2H_5)_2 + C_6H_5C(OC_2H_5)_2CH = CH_2.$$
(I)
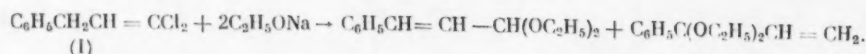
The yield of the second compound is the smaller.

The reaction with sodium n-butoxide takes a similar course. We assume an initial allylic prototropic rearrangement with formation of 1,1-dichlorophenylpropene-2:

$$C_6H_5CH_2CH = CCl_2 \xrightarrow{C_2H_5O^-} C_6H_5CH = CH - CHCl_2.$$
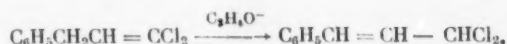
The 1,1-dichloro-3-phenylpropene-2 then reacts with sodium ethoxide in two ways: 1) without allylic isomerization with formation of cinnamaldehyde diethylacetal; 2) with allylic isomerization by the "reaction center transfer" mechanism [3] to give 1-chloro-3-ethoxy-3-phenylpropene-1. The latter compound in turn undergoes the allylic prototropic rearrangement and is converted into 1-chloro-3-ethoxy-3-phenylpropene-2, which reacts with sodium ethoxide to give (with allylic isomerization) the diethylketal of phenyl vinyl ketone:

$$C_6H_5CH = CH - CHCl_2 \xrightarrow{2C_2H_5ONa}$$

$$\nearrow C_6H_5CH = CH - CH(OC_2H_5)_2.$$

$$\searrow \left[\begin{array}{c} C_6H_5CH - CH = CHCl \\ | \\ OC_2H_5 \end{array} \right] \rightarrow \left[\begin{array}{c} C_6H_5C = CH - CH_2Cl \\ | \\ OC_2H_5 \end{array} \right] \rightarrow$$

(II)

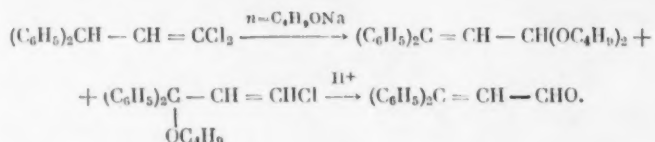$$\rightarrow C_6H_5C(OC_2H_5)_2CH = CH_2.$$

The reaction of 1,1-dichloro-3-phenylpropene-2 (II) with sodium methoxide or ethoxide was previously studied by Straus and Berkow [4] who only obtained 1-chloro-3-ethoxy-3-phenylpropene-2 by the action of one mole of sodium alkoxide; they did not observe the formation of cinnamaldehyde diethylacetal. By treating 1-chloro-3-ethoxy-3-phenylpropene-2 with another 2 moles of sodium ethoxide, Straus and Berkow converted it into the diethylketal of phenyl vinyl ketone. We reacted 1,1-dichloro-3-phenylpropene-2 with two moles of sodium ethoxide in absolute ethyl alcohol solution and found that, contrary to the findings of Straus and Berkow, a mixture of approximately equal amounts of cinnamaldehyde diethylacetal and phenyl vinyl ketone diethylketal is formed. It is still not clear why the reaction of 1,1-dichloro-3-phenylpropene-2 (II) with sodium ethoxide as

studied by Straus and Berkow should take a course different from that of our reaction and from that of the reaction of 1,1-dichloro-3-phenylpropene-1 (I) with sodium ethoxide if the latter also proceeds through 1,1-dichloro-3-phenylpropene-2 (II). In the case of the reaction of 1,1-dichloropropene-2 with sodium ethoxide, it was shown [5] that substitution with isomerization proceeds to the same extent as substitution without isomerization:
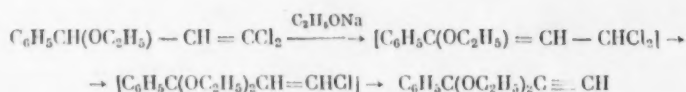
$$CH_2 = CH - CHCl_2 \xrightarrow{C_2H_5ONa} C_2H_5OCH_2CH = CHCl + CH_2 = CH - CH(OC_2H_5)_2.$$
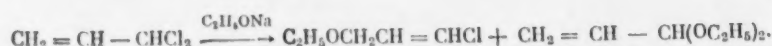
It would therefore appear that in the case of 1,1-dichloro-3-phenylpropene-2, in which the double bond is conjugated with the benzene ring, such a reaction course is even more probable. On this basis we think that our suggested course of the reaction of 1,1-dichloro-3-phenylpropene-1 with sodium ethoxide is the most probable. The structure of cinnamaldehyde diethylacetal was confirmed by its hydrogenation in ethyl alcohol solution over Pd/BaSO$_4$ to β-phenylpropionaldehyde diethylacetal which was identified as the 2,4-dinitrophenylhydrazone. The structure of phenyl vinyl ketone diethylketal was established in similar fashion. Reaction of 1,1-dichloro-2-methyl-3-phenylpropene-1 with sodium butoxide in n-butyl alcohol solution goes with formation of α-methylcinnamaldehyde dibutylacetal.

Treatment of 1,1-dichloro-3,3-diphenylpropene-1 with sodium butoxide gives a mixture of two compounds: 1-chloro-3-butoxy-3,3-diphenylpropene-1 and β-phenylcinnamaldehyde dibutylacetal. These are smoothly converted into β-phenylcinnamaldehyde on heating in acetic acid solution in presence of hydrochloric acid:

$$(C_6H_5)_2CH - CH = CCl_2 \xrightarrow{n-C_4H_9ONa} (C_6H_5)_2C = CH - CH(OC_4H_9)_2 +$$

$$+ (C_6H_5)_2C - CH = CHCl \xrightarrow{H+} (C_6H_5)_2C = CH - CHO.$$
$$\underset{OC_4H_9}{|}$$

The reaction with 1,1-dichloro-3-phenylbutene-1 goes in similar fashion. Reaction of 1,1-dichloro-3-ethoxy-3-phenylpropene-1 with sodium ethoxide gives only $C_6H_5C(OC_2H_5)_2C \equiv CH$, whose formation may be represented by the equation:

$$C_6H_5CH(OC_2H_5) - CH = CCl_2 \xrightarrow{C_2H_5ONa} [C_6H_5C(OC_2H_5) = CH - CHCl_2] \rightarrow$$

$$\rightarrow [C_6H_5C(OC_2H_5)_2CH=CHCl] \rightarrow C_6H_5C(OC_2H_5)_2C \equiv CH$$

The same compound is formed when sodium ethoxide acts on 1,1,1-trichloro-3-phenylpropene-2:

$$C_6H_5CH = CH - CCl_3 \xrightarrow{C_2H_5ONa} C_6H_5C(OC_2H_5)_2C \equiv CH.$$
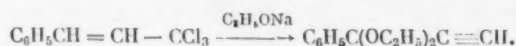
It forms a silver salt with an alcoholic solution of silver nitrate; hydrogenation converts it into propiophenone diethylketal. An interesting feature of the reaction of 1,1-dichloro-3-ethoxy-3-phenylpropene-1 is the reaction of 1,1-dichloro-3-ethoxy-3-phenylpropene-2 (formed intermediately by the allylic prototropic rearrangement) with sodium ethoxide solely by the "reaction center transfer" mechanism. In an acid medium, as was shown earlier [6], 1,1-dichloro-3-ethoxy-3-phenylpropene-1 undergoes the allylic anionotropic rearrangement and is converted into cinnamic acid.

EXPERIMENTAL

Action of sodium ethoxide on 1,1-dichloro-3-phenylpropene-1. 30 g of 1,1-dichloro-3-phenylpropene-1 was gradually added to a heated solution of 11.2 g of sodium in 140 ml of absolute ethyl alcohol. The mixture came to the boil. After completion of the addition, the reaction mass was heated for 2 hrs on a water bath and the alcohol was distilled off in vacuo. Water was added to the residue to dissolve the salts. The layer of oil was extracted with benzene and dried over potassium carbonate. Vacuum distillation gave 11.4 g of fraction I with

b. p. 76-84° (2 mm) and 15.1 g of fraction II with b. p. 100-108° (2 mm). Redistillation of fraction I gave phenyl vinyl ketone diethylketal with b. p. 77-78° (2 mm); n_D^{20} 1.4960; d_4^{20} 0.9744.

Found %: C 75.79, 75.62; H 8.47, 8.53. $C_{13}H_{18}O_2$. Calculated %: C 75.72; H 8.73.

Redistillation of fraction II gave cinnamaldehyde diethylacetal with b. p. 105-106° (2 mm); n_D^{20} 1.5140; d_4^{20} 0.9804. Literature data: b. p. 140-142° (12 mm); d_4^{15} 0.981 [7]. On treatment with 2,4-dinitrophenylhydrazine (2,4-DPH) the acetal gave cinnamaldehyde 2,4-dinitrophenylhydrazone with m. p. 250° (from glacial acetic acid). The acetal did not give a depression of melting point in a mixed test with an authentic specimen. Hydrogenation of 2 g of cinnamaldehyde diethylacetal in alcoholic solution over 0.1 g of 5% Pd/BaSO₄ gave β-phenylpropionaldehyde diethylacetal; treatment of the latter with 2,4-DPH gave the 2,4-dinitrophenylhydrazone of β-phenylpropionaldehyde with m. p. 158-159° (from glacial acetic acid). It did not give a depression of melting point in a mixed test with an authentic specimen. Literature data: m. p. 158° [8]. 2.3 g of phenyl vinyl ketone diethylketal was hydrogenated over 0.1 g of 5% Pd/BaSO₄. After the catalyst had been removed, a portion of the alcoholic solution was treated with 2,4-DPH to give propiophenone 2,4-diphenylhydrazone with m. p. 189-190° (from glacial acetic acid). The compound did not give a depression of melting point in admixture with an authentic specimen. Literature data: m. p. 190° [9].

Action of sodium butoxide on 1,1-dichloro-3-phenylpropene-1. 20 g 1,1-dichloro-3-phenylpropene-1 was gradually added to a heated solution of 6 g of sodium in 130 ml of n-butyl alcohol. The reaction proceeded vigorously with boiling of the butyl alcohol. The mixture was then heated for an hr. Water was added to the cooled mixture, and the butyl alcohol layer was collected and dried over potassium carbonate. Distillation in vacuo gave 8.5 g of phenyl vinyl ketone dibutylketal with b. p. 110-112° (2 mm); n_D^{20} 1.4925; d_4^{20} 0.9420.

Found %: C 77.80, 77.98; H 9.74, 9.82. $C_{17}H_{26}O_2$. Calculated %: C 77.86; H 9.92.

There was also obtained 13.5 g of cinnamaldehyde dibutylacetal with b. p. 138-140° (2 mm); n_D^{20} 1.5040; d_4^{20} 0.9454.

Found %: C 77.88, 77.87; H 9.71, 9.82. $C_{17}H_{26}O_2$. Calculated %: C 77.86; H 9.92.

1,1-Dichloro-2-methyl-3-phenylpropene-1. 1.5 g of anhydrous aluminum chloride was gradually added to a solution of 30 g of 1,1,3-trichloro-2-methylpropene in 80 ml of benzene. Hydrogen chloride came off in large volume and appreciable heat was liberated. After hydrogen chloride had ceased to come off, the reaction mass was decomposed with water. The benzene solution was dried over calcium chloride. Distillation in vacuo gave 22.1 g of 1,1-dichloro-2-methyl-3-phenylpropene-1 with b. p. 75-76° (2 mm); n_D^{20} 1.5421.

Found %: C 59.88, 59.92; H 4.93, 4.82. $C_{10}H_{10}Cl_2$. Calculated %: C 59.70; H 4.97.

Action of sodium butoxide on 1,1-dichloro-2-methyl-3-phenylpropene-1. 19.5 g of 1,1-dichloro-2-methyl-3-phenylpropene-1 and a solution of 5.5 g of sodium in 110 ml of butyl alcohol were refluxed for 4 hrs. After the mass had been worked up in the usual manner, 7.2 g of a fraction with b. p. 95-140° (2 mm) was obtained; this was treated with 2,4-DPH to give α-methylcinnamaldehyde 2,4-dinitrophenylhydrazone with m. p. 208-209° (from glacial acetic acid) and 10.1 g of α-methylcinnamaldehyde dibutylacetal with b. p. 145-146° (2 mm); n_D^{20} 1.5000; d_4^{20} 0.9425.

Found %: C 78.21, 77.87; H 10.05, 10.04. $C_{18}H_{28}O_2$. Calculated %: C 78.25; H 10.14.

The dibutylacetal gave a semicarbazone with m. p. 207-208° (from aqueous alcohol). Literature data: m. p. 207-208° [10]. Treatment with 2,4-DPH gave α-methylcinnamaldehyde 2,4-dinitrophenylhydrazone with m. p. 208-209° (from glacial acetic acid).

Found %: N 17.32, 17.40. $C_{16}H_{14}N_4O_4$. Calculated %: N 17.17.

<u>Action of sodium butoxide on 1,1-dichloro-3-diphenylpropene-1.</u> 14 g of 1,1-dichloro-3,3-diphenylpro-pene-1 was heated with a solution of 3 g of sodium in 60 ml of butyl alcohol; the reaction mixture was worked up in the usual manner to give a mixture of 1-chloro-3-butoxy-3,3-diphenylpropene-1 and β-phenylcinnamalde-hyde dibutylacetal; the latter was isolated in the pure form; b. p. 178-179° (2.5 mm); n_D^{20} 1.5415; d_4^{20} 0.9984.

Found %: C 82.03, 82.08; H 8.75, 9.01. $C_{23}H_{30}O_2$. Calculated %: C 81.65; H 8.87.

Treatment with 2,4-DPH gave the 2,4-dinitrophenylhydrazone with m. p. 196-197° (from glacial acetic acid).

Heating of the same mixture in acetic acid solution in presence of a little hydrochloric acid on a water bath for an hour gave 8.1 g (73% of the theoretical) of β-phenylcinnamaldehyde. The 2,4-dinitrophenylhydra-zone melted at 196-197°. The literature reports 196-197° [2].

Heating of 4.8 g of 1,1-dichloro-3-phenylbutene-1 [12] with a solution of 1.1 g of sodium in 30 ml of butyl alcohol similarly gave a mixture of reaction products which on treatment with 2,4-DPH in an acid medium gave β-methylcinnamaldehyde 2,4-dinitrophenylhydrazone with m. p. 209-210° (from glacial acetic acid). The litera-ture gives m. p. 211° [12].

<u>Action of sodium ethoxide on 1,1-dichloro-3-ethoxy-3-phenylpropene-1.</u> 15 g of 1,1-dichloro-3-ethoxy-3-phenylpropene-1 and a solution of 4.5 g of sodium in 70 ml of absolute ethyl alcohol were heated on a water bath for 4 hrs. The mixture was run into water and the oil layer was extracted with ether. The ethereal solution was dried over potassium carbonate. Distillation in vacuo gave 10.7 g of phenyl ethynyl ketone diethylketal with b. p. 80-81° (2 mm); n_D^{20} 1.5072; d_4^{20} 1.0085.

Found %: C 76.25, 76.48; H 7.77, 7.52. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.84.

Treatment with an alcoholic solution of silver nitrate gave a silver salt; treatment with 2,4-DPH gave the 2,4-dinitrophenylhydrazone with m. p. 114.5-115° (from glacial acetic acid).

Found %: N 18.36, 18.43. $C_{15}H_{10}N_4O_4$. Calculated %: N 18.06.

Hydrogenation in alcoholic solution over 5% Pd/BaSO$_4$ gave propiophenone, which formed the 2,4-dinitrophenyl-hydrazone on treatment with 2,4-DPH; m. p. 189-190°. No depression of melting point in admixture with an authentic specimen.

<u>Action of sodium ethoxide on 1,1,1-trichloro-3-phenylpropene-2.</u> 8 g of 1,1,1-trichloro-3-phenylpropene-2 was gradually added to a solution of 3.5 g of sodium in 40 ml of absolute alcohol. Heat was developed. After heating on a water bath for 4 hrs, the reaction mass was worked up as in the preceding experiment to give 4.7 g of phenyl ethynyl ketone diethylketal (n_D^{20} 1.5070); it forms a silver salt and gives a 2,4-dinitrophenylhydrazone with m. p. 114-115°, identical with that prepared in the preceding experiment.

SUMMARY

1. Under the action of sodium alkoxide, 1,1-dichloro-3-phenylpropene-1 undergoes the allylic prototropic rearrangement to 1,1-dichloro-3-phenylpropene-2, which reacts with the sodium alkoxide to form cinnamaldehyde diethylacetal and phenyl vinyl ketone diethylketal.

2. Sodium ethoxide reacts with 1,1-dichloro-3-ethoxy-3-phenylpropene-1 to give phenyl ethynyl ketone diethylketal.

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POLYMERIZATION OF CHLOROPHENYL ESTERS OF METHACRYLIC ACID

I. A. Arbuzova and L. I. Medvedeva

Processes of polymerization of chloro-substituted phenyl esters of methacrylic acid are the subject of the present investigation. Although many papers have described the synthesis of various esters of acrylic and methacrylic acids, little work has hitherto been carried out on their polymerization. Only the mechanism and kinetics of polymerization of methyl methacrylate have been closely investigated [1-5].

According to the literature the character of the dependence of the rate of polymerization on the degree of transformation of methyl methacrylate is different from that of the majority of other vinyl monomers; investigation of the kinetics of its polymerization also indicates the occurrence of a self-accelerating step after the reaction has proceeded to the extent of 20-30%, and is accounted for by a fall in the velocity constant of chain rupture due to increase in the viscosity of the medium [5]. A self-accelerating step was also observed with other esters of methacrylic acid [6]. In explanation of the differing behavior of different vinyl compounds during polymerization, Shantorovich and Medvedev suggested that the kinetics of polymerization at a high degree of transformation are governed by the structure of the polymer formed [7].

The velocity constant of chain rupture is reduced when polymerization proceeds with development of kinetic branching reactions. If branches are not formed, the velocity constant remains unaltered independently of the degree of polymerization, and the reaction rate (which in this case is governed solely by the concentration of the monomer in the system) falls continuously. In the authors' opinion, branches are formed during polymerization of compounds containing the conjugated C=C−C=O group, and is associated with opening of the C=O double bond. At the same time, the increased polymerization rate (the "gel effect") is also observed to a lesser degree with vinyl compounds not containing the C=C−C=O grouping: with vinyl acetate [8, 9] (the gel effect was reduced in work with shorter polymer radicals), styrene [9], and vinyl chloride [10]. Further study of processes of polymerization both of compounds containing the C=C−C=O grouping and of those not containing the grouping will provide experimental material for a solution of the problem of the nature of the kinetics of polymerization of various vinyl compounds.

We studied the polymerization of p-chloro-, 2,4-dichloro- and 2,4,6-trichlorophenyl esters of methacrylic acid. The picture of the kinetics of polymerization of chlorophenyl esters is similar to that of the polymerization of methyl methacrylate. A linear reaction period at the start is followed by a sudden acceleration accompanied by a rise in molecular weight of the polymer formed. Chlorophenyl esters of methacrylic acid were block-polymerized at 70° (±0.2°) with ~ 0.1 mole% of benzoyl peroxide. The course is plotted in Fig. 1 in which the rate of polymerization of methyl methacrylate under similar conditions is also plotted for comparison.

Figure 1 shows that the rate of polymerization of chlorophenyl esters of methacrylic acid is higher than that of methyl methacrylic but is substantially completed at about 80% conversion, whereas the conversion of methyl methacrylate reaches 95%. Determination of the characteristic viscosity of poly-p-chlorophenyl methacrylate also revealed an appreciable increase in molecular weight during the acceleration of the reaction. The curve of polymerization of p-chlorophenyl methacrylate and the change of the characteristic viscosity are plotted in Fig. 2.

Characteristic viscosities of the polymer of 2,4,6-trichlorophenyl methacrylate in dependence on the degree of conversion are listed in Table 1.
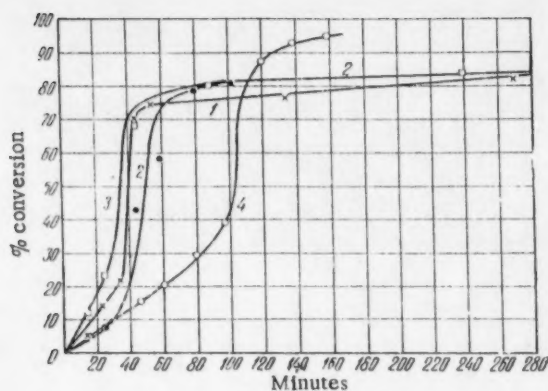
Fig. 1. Polymerization curves of chlorophenyl esters of methacrylic acid: 1) p-chlorophenyl methacrylate; 2) 2,4-dichlorophenyl methacrylate; 3) 2,4,6-trichlorophenyl methacrylate; 4) methyl methacrylate.
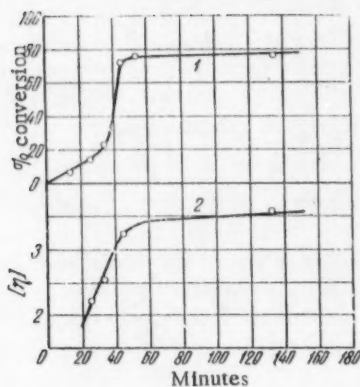

Fig. 2. Curves: 1) polymerization of p-chlorophenyl methacrylate (0.0812 mole% benzoyl peroxide, 70°); 2) change of characteristic viscosity.

TABLE 2

Characteristic Viscosity of p-Chlorophenyl Methacrylate Polymer

Duration of poly-merization in min	Degree of conversion in %	[η]
45	10.13	3.98
70	15.2	3.87
103	44.53	4.60
132	56.26	4.50
245	68.9	4.55
1440	86.70	4.62

TABLE 1

Characteristic Viscosity of the Polymer of 2,4,6-Trichlorophenyl Methacrylate

Duration of poly-merization in min	Degree of conversion in %	[η]
15	12.2	1.40
25	23.5	1.26
600	87.0	1.22

The low values of characteristic viscosity and their decrease during the polymerization were evidently the consequence of the high reaction rate which led to local overheating of the reaction mass.

On the analogy of the chlorinated sytrenes [11, 12] we argued that the rate of polymerization would be influenced by the differing amounts of chlorine in the phenyl ring of the various esters of methacrylic acid selected for the investigation. This effect is not manifested, however, in the series of experiments whose results are plotted in Fig. 1. On the assumption that this effect was masked by the high reaction rates and the rapidly commencing acceleration in the case of polymerization of 2,4,6-trichlorophenyl methacrylate, a consequence of which was the low viscosity of the medium, we carried out a second series of experiments in presence of a smaller quantity of initiator. The curves in Fig. 3 relate to p-chloro-, 2,4-dichloro- and 2,4,6-trichlorophenyl methacrylates obtained by block polymerization in presence of 0.01607 mole% of benzoyl peroxide.
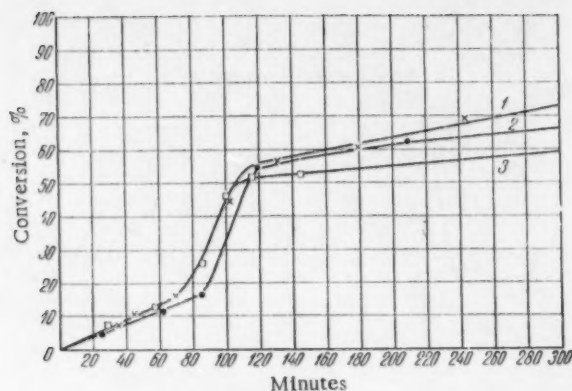
Fig. 3. Polymerization curves of p-chloro-, 2,4-dichloro- and 2,4,6-trichlorophenyl methacrylates: 1) p-chlorophenyl methacrylate; 2) 2,4-dichlorophenyl methacrylate; 3) 2,4,6-trichlorophenyl methacrylate.
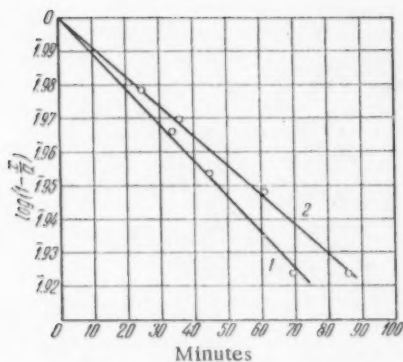

Fig. 4. Relation between logarithm of concentration and time: 1) p-chlorophenyl methacrylate (0.01607 mole% of benzoyl peroxide, 70°); 2) 2,4-dichlorophenyl methacrylate (0.01607 mole% benzoyl peroxide, 70°).
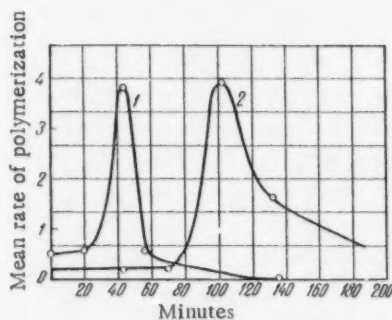

Fig. 5. Relation between mean rate of polymerization of p-chlorophenyl methacrylate and time at 70°: curve 1: 0.0812 mole% benzoyl peroxide; curve 2: 0.01607 mole% benzoyl peroxide.

We see that all of the three esters undergo an initial linear period of reaction until conversion is about 15%. During this period the reaction is first order (Fig. 4). The velocity constants have the following values: p-chlorophenyl methacrylate $K_1 = 0.388 \cdot 10^{-4}$ sec^{-1}; 2,4-dichlorophenyl methacrylate $K_1 = 0.304 \cdot 10^{-4}$ sec^{-1}; 2,4,6-trichlorophenyl methacrylate $K_1 = 0.404 \cdot 10^{-4}$ sec^{-1}. This is followed by acceleration until conversion is 50-55%. Unlike the polymerization of methyl methacrylate, that of the chlorophenyl esters continues with appreciable speed also after the end of the self-accelerating period. The influence of replacement of hydrogen by chlorine in the phenyl nucleus is manifested in an earlier termination of the self-acceleration period and in a smaller percentage conversion with increasing chlorine content. Table 2 gives the characteristic viscosities of p-chlorophenyl methacrylate polymer obtained at 70° with 0.01670*mole% of initiator. The molecular weight of the polymer is seen to increase during the period of acceleration of the reaction.

In Fig. 5 the mean rate of polymerization is plotted against time; an approximately fourfold increase in reaction rate is indicated.

The rate of polymerization of p-chlorophenyl methacrylate is plotted against the quantity of initiator in Fig. 6; the curves show an earlier termination of the self-acceleration period when the polymerization is carried

* Probably 0.01607 — Publisher's note.

TABLE 3

Polymerization of Chlorophenyl Esters of Methacrylic Acid at 70°

p-Chlorophenyl methacrylate (amount of benzoyl peroxide 0.0812 mole%)			2,4-Dichlorophenyl methacrylate (0.0953 mole% benzoyl peroxide)			2,4,6-Trichlorophenyl methacrylate (0.1098 mole% benzoyl peroxide)		
Duration in min	Degree of conversion in %	Rate of polymerization in min	Duration in min	Degree of conversion in %	Rate of polymerization in min	Duration in min	Degree of conversion in %	Rate of polymerization in min
15	5.79	0.38	25	8.05	0.32	15	12.2	0.83
25	14.11	0.83	35	33.1	2.50	25	23.5	1.13
35	21.85	0.77	45	43.3	1.02	45	68.6	2.87
45	70.50	4.86	60	58.4	1.00	90	80.0	0 25
55	74.17	0.36	80	78.4	1.00	240	84.1	0.027
135	76.12	0.024	102	81.0	0.12	600	87.0	0.008
270	82.31	0.045	600	90.8	0.02	1440	87.7	—
1560	87.88	—	1440	93.0	—	—	—	—

TABLE 4

Polymerization of Chlorophenyl Esters of Methacrylic Acid

Duration in min	Degree of conversion in %	Rate of polymerization in min	Acceleration	$K \cdot 10^{-4} \ \mathrm{sec}^{-1}$	$\log\left(1 - \frac{x}{a}\right)$
Polymerization of p-chlorophenyl methacrylate (temperature 70°, 0.01607 mole% benzoyl peroxide)					
34	7.4	0.22	—	0.376	$\overline{1}.96661$
45	10.1	0.24	—	0.393	$\overline{1}.95376$
70	16.0	0.24	—	0.396	$\overline{1}.92376$
103	44.5	0.86	3.9	—	—
132	56.3	0.4	1.36	—	—
245	69.0	0.11	.0.5	—	—
560	84.6	0.05	0.23	—	—
1440	86.7	0.0026	0.01	—	—
Polymerization of 2,4-dichlorophenyl methacrylate (temperature 70°, 0.01607 mole% benzoyl peroxide)					
25	4.7	0.19	—	0.321	$\overline{1}.97909$
36	6.5	0.16	—	0.274	$\overline{1}.97081$
62	11.1	0.18	—	0.316	$\overline{1}.94890$
86	16.1	0.20	—	0.339	$\overline{1}.92376$
120	54.3	1.12	6.8	—	—
180	60.9	0.2	1.0	—	—
210	62.4	0.05	0.26	—	—
600	76.9	—	—	—	—
1440	78.3	—	—	—	—
Polymerization of 2,4,6-trichlorophenyl methacrylate (temperature 70°, 0.01607 mole% benzoyl peroxide)					
57	13.0	0.23	—	0.404	—
86	26.4	0.44	1.9	—	—
101	45.8	1.3	5.6	—	—
115	51.7	0.42	1.8	—	—
145	52.3	0.02	0.009	—	—
745	75.8	0.04	—	—	—

TABLE 5

Characteristic Viscosity of Poly-p-chlorophenyl Methacrylate in Dependence on the Period of Polymerization

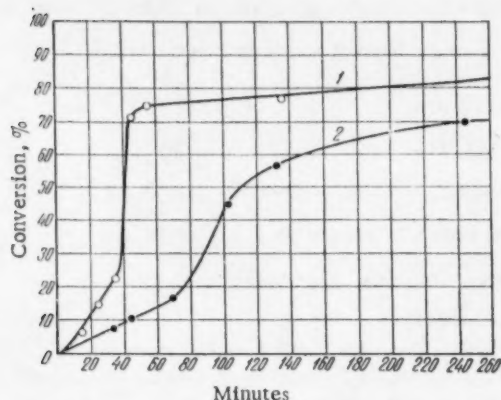| Duration of polymerization in min	Degree of conversion, %	Concentration in g/liter	η_{spec}/c	$[\eta]_{c\to 0}$
Temperature 70°, 0.0812 mole% benzoyl peroxide				
25	14.11	6.344	3.82	
		3.172	3.15	
		1.586	2.73	
		0.793	2.49	
		0.397	2.35	2.28
35	21.85	8.012	4.91	
		4.006	3.74	
		2.003	3.09	
		1.000	2.86	
		0.500	2 72	2.56
45	70.55	5.096	6.29	
		2.548	4.64	
		1.274	3.93	
		0.637	3.59	
		0.318	3.31	3.24
135	76.12	4.890	5.74	
		2.445	4.45	
		1.222	4.00	
		0.611	3.80	3.57
270	82.31	5.122	6.84	
		2.561	5.09	
		1.280	4.44	
		0.640	4.20	
		0.320	3.78	3.65
Temperature 70°, 0.01607 mole% benzoyl peroxide				
45	10.13	2.525	5.88	
		1.262	5.03	
		0.631	4.37	3.98
70	15.2	2.571	5.88	
		1.430	4.85	
		0.715	4.40	
		0.357	4.00	3.87
103	44 53	5.000	9.44	
		2.500	6.70	
		1.250	5.55	
		0.625	5.20	
		0.3125	5.00	4.60
132	56.26	3.432	8.03	
		1.716	6.06	
		0.858	5.34	
		0.420	4.96	4.50
245	68.98	3.336	7.87	
		1.516	5.96	
		0.758	5.31	
		0.379	4.82	4.55
1440	86.71	3.718	8.22	
		1.859	6.36	
		0.929	5.61	
		0.465	5.31	4.62

Fig. 6. Relation between speed of polymerization of p-chlorophenyl methacrylate and the quantity of initiator: 1) 0.0812 mole % benzoyl peroxide; 2) 0.01607 mole% benzoyl peroxide.

out with a smaller quantity of initiator.* Examination of the characteristic viscosities of polymers (Fig. 2 and Table 2) enables us to postulate that the cause of the earlier termination of the self-acceleration period is the higher viscosity of the reaction medium when operating with a small quantity of benzoyl peroxide. In conjunction with the reduced mobility (relative to methyl methacrylate) of the monomer with its bulky chlorophenyl groups, this leads to a more pronounced retardation of diffusion of the monomer toward the growing end of the radical, and in turn to earlier termination of the self-acceleration period. In presence of a large quantity of monomer in the polymerizing mixture, the termination of the self-acceleration period (in the case of reaction with a smaller quantity of initiator) does not lead to termination of polymerization, as is the case with methyl methacrylate, but only to its retardation. Further heating at a constant temperature leads to the monomer diffusing (although slowly) toward the growing end of the polymer chain, and the conversion increases by 25-30 % but still remains 10% less than in the case of methyl methacrylate.

Consequently, the study of the kinetics of polymerization of chlorophenyl esters of methacrylic acid has established that the reaction includes a period of self-acceleration. The rate and character of the polymerization are also seen to be influenced by the replacement of the methyl group by the bulkier chlorophenyl group.

EXPERIMENTAL

The monomers (chlorinated esters of methacrylic acid) were prepared by reaction of the corresponding chlorophenol with methacrylyl chloride by our previously described procedure [13]. Prior to polymerization, the p-chlorophenyl methacrylate with b. p. 113-114° (6 mm) was further purified by washing first with 4% sodium hydroxide solution and then with water, and finally dried with calcium chloride. Crystalline 2,4-dichloro- and 2,4,6-trichlorophenyl methacrylates were purified by repeated crystallization from a mixture of alcohol and benzene. After further purification, p-chlorophenyl methacrylate had d_4^{20} 1.1788; n_D^{20} 1.5289; 2,4-dichlorophenyl methacrylate had m. p. 55.5-56°; 30.51% Cl; calculated for $C_{10}H_8O_2Cl_2$ 30.70% Cl; 2,4,6-trichlorophenyl methacrylate had m. p. 61-61.5°; 40.14% Cl; calculated for $C_{10}H_7O_2Cl_3$ 40.08% Cl.

Polymerization was carried out in ampoules with two branches with a volume of 2-2.5 ml. A stream of oxygen-free nitrogen was passed into the ampoules for 25-30 min before sealing. We did not observe an inhibition of the reaction when polymerization was carried out under these conditions. The degree of conversion was determined by precipitation of the reaction mixture (dissolved in dioxan) into methyl alcohol, redissolution of the polymer in dioxan , and reprecipitation into methyl alcohol. The characteristic viscosity was determined in dioxan solution in an Ostwald type viscometer. Results of polymerization experiments are presented in Tables 3 and 4; viscosity measurements are in Table 5.

SUMMARY

1. The kinetics of the polymerization of p-chloro-, 2,4-dichloro- and 2,4,6-trichlorophenyl methacrylates are similar in character to those of the polymerization of methyl methacrylate: an initial linear reaction period is followed by a sudden acceleration of polymerization accompanied by an increase in molecular weight of the polymer.

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* According to the data of Schulz and Harbort [5] the quantity of initiator has no appreciable influence upon the degree of conversion of methyl methacrylate.

2. The influence of the chlorine in the phenyl ring of the methacrylic ester is manifested in a lower degree of conversion and in an earlier termination of the period of self-acceleration with increasing chlorine content.

3. Replacement of the methyl group of methacrylic ester by the bulkier chlorophenyl group is reflected in a higher reaction rate and in stoppage of polymerization after a lower degree of conversion.

4. A theory of the causes of these phenomena is advanced on the basis of the experimental data.

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* In Russian.
** Original Russian pagination. See C. B. translation.

SYNTHESIS OF AMINOALKYLPHOSPHONIC ACIDS

THE REACTION OF SOME HETEROCYLIC KETONES WITH DIALKYLPHOSPHITES AND AMMONIA
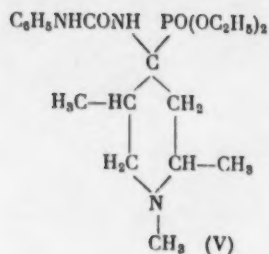
T. Ya. Medved and M. I. Kabachnik

We previously showed that reaction of aldehydes or ketones with dialkyl phosphites and ammonia leads to formation of esters of α-aminoalkylphosphonic acids [1]. In the present work we investigated the possibility of extending this reaction to heterocyclic ketones. As starting substances we selected 1,2,5-trimethyl-4-piperidone (now readily accessible thanks to the recent work of Nazarov and Rudenko [2]) and 2,2-dimethyltetrahydropyran-4-one. We found that these ketones readily enter into reaction with dialkyl phosphites and ammonia to form the corresponding esters of 1,2,5-trimethyl-4-aminopiperidine-4-phosphonic acid (I) and(III) and of 2,2-dimethyl-4-aminotetrahydropyran-4-phosphonic acid (II).
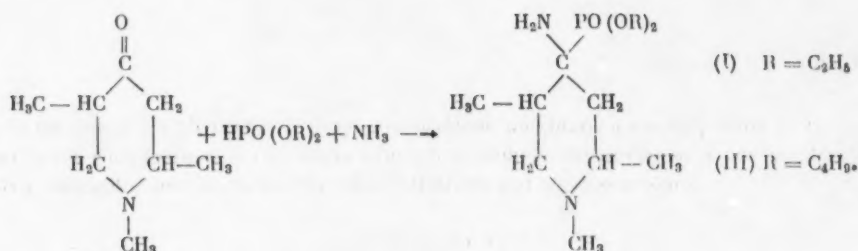
The ester of aminothiophosphonic acid (IV) was isolated on carrying out the reaction with diethyl thiophosphite.

(II)   (IV)
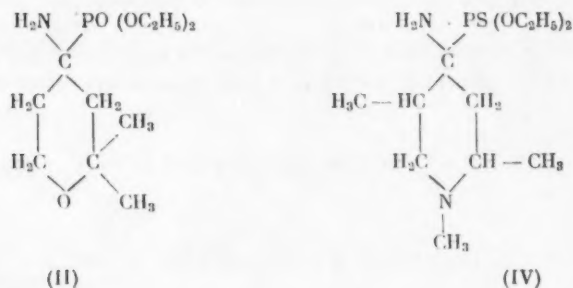
The esters of aminophosphonic acids are mobile, yellowish liquids with a faint characteristic odor; they are extremely hygroscopic, readily soluble in organic solvents, possess basic properties and form readily crystallizing phosphates. They react at the free amino group with phenyl isocyanate to form the corresponding ureas, for example, (V):

$$C_6H_5NHCONH \quad PO(OC_2H_5)_2$$

$$\underset{\underset{\overset{|}{CH_3} \quad (V)}{\overset{|}{N}}}{\underset{H_2C \quad CH-CH_3}{\overset{H_3C-HC \quad CH_2}{\overset{C}{}}}}$$

The structural similarity between the compounds synthesized and a group of well-known analgesics [3] makes it of interest to synthesize their acetyl, propionyl and benzoyl derivatives. It was found that reaction of acetyl chloride or acetic anhydride, propionyl chloride and benzoyl chloride with esters of 1,2,5-trimethyl-4-amino-piperidyl-4-phosphonic acid gives the acid chloride of the respective acyl derivatives, which on treatment with sodium carbonate form the free acyl derivatives (VI), (VII) and (VIII)

$$\underset{\overset{|}{CH_3}}{\overset{H_2N \quad PO(OR)_2}{C}} \quad \xrightarrow{R'COCl} \quad \underset{\overset{|}{CH_3}}{\overset{R'CONH \quad PO(OR)_2}{C}} \cdot HCl \quad \xrightarrow{Na_2CO_3}$$

$$\xrightarrow{Na_2CO_3} \quad \underset{\overset{|}{CH_3}}{\overset{R'CONH \quad PO(OR)_2}{C}}$$

$R = C_2H_5;$ (VI) $R' = CH_3;$ (VII) $R' = C_2H_5;$ (VIII) $R' = C_6H_5;$
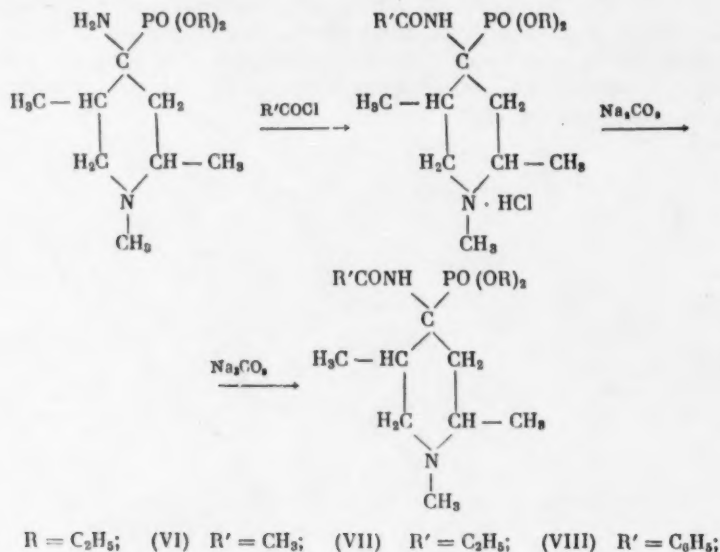
In similar fashion we prepared the ethyl ester of 2,2-dimethyl-4-propionylaminotetrahydropyran-4-phosphonic acid (IX)

$$C_2H_5CONH \quad PO(OC_2H_5)_2$$

(IX)
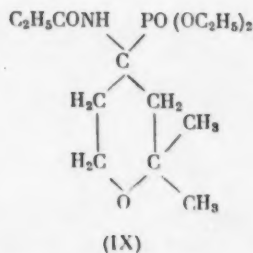
All of the acyl derivatives are colorless, crystalline substances, readily soluble in organic solvents and in water.

In order to establish the influence of the acylamino group on the physiological activity of the compounds, we synthesized esters of the corresponding acyloxyphosphonic acids. For this purpose we made use of the Abramov reaction [4] — the action of dialkyl phosphites on ketones in presence of sodium alkoxide. In our case the reaction proceeds with sufficient facility and corresponds to the scheme:

(X)

(XI)
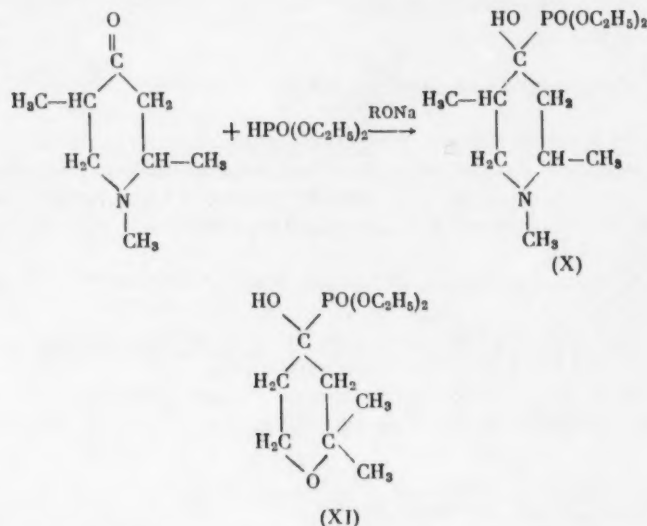
Thus in the reaction with 1,2,5-trimethyl-4-piperidone we obtained the ethyl ester of 1,2,5-trimethyl-4-hydroxypiperidyl-4-phosphonic acid (X), while with 2,2-dimethyltetrahydropyran-4-one we obtained ester (XI). The latter is a crystalline substance, readily soluble in water and organic solvents.

EXPERIMENTAL

Ethyl ester of 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonic acid (I). A stream of dry gaseous ammonia was passed into a mixture of 18 g (0.127 mole) of 1,2,5-trimethyl-4-piperidone* and 17.5 g (0.127 mole) of diethyl phosphite. The temperature rose to 40° during this operation. The reaction mixture was thereupon heated (with constant flow of ammonia) for 3 hrs at 50° and for 2 hrs on a boiling water bath. After cooling of the reaction mixture, dry ether was introduced until precipitation ceased. The precipitate (mainly the ammonium salt of ethyl phosphite) was filtered off, the ethereal filtrate was dried, the ether was driven off, and the residue was distilled in vacuo. Two distillations gave a fraction with b. p. 136-137.5° (2 mm); 15.2 g (43%); a transparent, pale-yellow, hygroscopic liquid with a weak odor; b. p. 81-83° (0.1 mm); n_D^{20} 1.4784; d_4^{20} 1.0601; found MR 73.9; calculated MR 73.6.

Found %: C 51.8, 51.7; H 10.0; 9.9; N 10.2, 10.2; P 11.2, 11.3. $C_{12}H_{27}O_3N_2P$. Calculated %: C 51.8; H 9.8; N 10.1; P 11.2.

Picrate of ethyl ester of 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonic acid. M. p. 165-166° after recrystallization from absolute alcohol.

Found %: C 39.0, 38.8; H 4.7, 4.8; N 15.0, 14.9; P 3.7, 3.8. $C_{24}H_{33}N_8PO_{17}$. Calculated %: C 39.1; H 4.5; N 15.2; P 4.2.

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* The technical product was dried in ethereal solution over sodium sulfate, and then distilled in vacuo; b. p. 49-50° (3 mm); n_D^{20} 1.4590; d_4^{20} 0.9415.

Ethyl ester of 2,2-dimethyl-4-aminotetrahydropyran-4-phosphonic acid (II). Prepared from 12.8 g (0.1 mole) of 2,2-dimethyltetrahydropyran-4-one [b. p. 48-52° (3 mm); n_D^{20} 1.4483; d_4^{20} 0.9926], 13.8 g (0.1 mole) of diethyl phosphite and dry ammonia. Yield 15 g (56%) of a yellowish, oily liquid with b. p. 79-81° (0.01 mm); n_D^{20} 1.4691; d_4^{20} 1.1088; found MR 66.66; calculated MR 66.7. The substance is hygroscopic.

Found %: N 5.0, 5.1; P 11.2, 11.3. $C_{11}H_{24}O_4NP$. Calculated %: N 5.3; P 11.7.

Butyl ester of 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonic acid (III). Prepared from 14.1 g (0.1 mole) of 1,2,5-trimethyl-4-piperidone, 19.4 g (0.1 mole) of dibutyl phosphite and dry ammonia. Fractionation gave a fraction with b. p. 108-109° (4·10^{-4} mm); yellowish liquid; n_D^{20} 1.4693; d_4^{20} 1.0240; found MR 91.0; calculated MR 92.1; yield 17.5 g (52%).

Found %: P 9.2, 9.3. $C_{16}H_{35}O_3N_2P$. Calculated %: P 9.3.

Ethyl ester of 1,2,5-trimethyl-4-aminopiperidyl-4-thiophosphonic acid (IV). Prepared from 7.1 g (0.05 mole) of 1,2,5-trimethyl-5-piperidone, 7.7 g (0.05 mole) of diethyl thiophosphite and dry ammonia. Fractionation of the reaction products gave a fraction with b. p. 120-123° (3 mm); a transparent, yellowish liquid; n_D^{20} 1.4952; d_4^{20} 1.0720; found MR 80.1; calculated MR 80.1; yield 6.1 g (42%).

Found %: C 49.3, 49.2; H 9.3, 9.3; P 10.6, 10.7. $C_{12}H_{27}O_2N_2SP$. Calculated %: C 48.9; H 9.3; P 10.5.

Ethyl ester of 1,2,5-trimethyl-4-(N-phenylureido)-piperidyl-4-phosphonic acid (V). 0.8 g (0.007 mole) of phenyl isocyanate was added to 1.4 g (0.005 mole) of the ethyl ester of 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonic acid; the temperature of the reaction mixture rose to 50°, after which the mixture was heated for 3 min on a boiling water bath. The mixture crystallized on cooling. Yield 1.85 g of substance; m. p. (from benzene) 198°.

Found %: P 8.2, 8.2. $C_{19}H_{32}O_4N_3P$. Calculated %: P 7.8.

Ethyl ester of 1,2,5-trimethyl-4-acetaminopiperidyl-4-phosphonic acid (VI). A) A solution of 1 g of acetyl chloride in 2 ml of ligroine was added with stirring to 2.8 g (0.01 mole) of (I) in 30 ml ligroine at such a speed that the temperature of the reaction mixture did not rise above 20-25°. When all had been added, stirring was continued for another hour after which the precipitate was filtered in a current of dry air. The product was a hygroscopic substance that deliquesced in the air; readily soluble in alcohol, acetone and chloroform; insoluble in ethyl ether and ligroine in benzene. It was dried over calcium chloride and paraffin wax; the yield was 3.3 g (92%); decomp. temperature 104°.

Found %: P 8.7, 8.4; Cl 10.3, 10.3. $C_{14}H_{29}N_2PO_4 \cdot HCl$. Calculated %: P 8.7; Cl 9.6.

5.4 g of the hydrochloride, prepared as described above, was neutralized with saturated aqueous sodium carbonate, and the solution was extracted with ether. The ethereal extracts were dried over sodium sulfate, the ether was driven off, and the residue was distilled in vacuo. 1.55 g (33%) of product came over at 127° (2·10^{-4} mm) and soon crystallized. The crystals were washed with ligroine and dried over a paraffin wax; m. p. 115-117°.

Found %: C 52.7, 52.8; H 9.3, 9.4; N 8.8, 8.9; P 9.8, 9.9. $C_{14}H_{29}N_2PO_4$. Calculated %: C 52.5; H 9.1; N 8.8; P 9.7.

B) 5 g of acetic anhydride was stirred into 2.8 g (0.01 mole) of compound (I), after which the mixture was heated for 10 min on a boiling water bath. The excess of acetic anhydride was distilled off, and the residue neutralized with saturated sodium carbonate solution. The aqueous solution was extracted with ether, the ethereal solution was dried with sodium sulfate, the ether was distilled off, and the residue was distilled in vacuo. 1.8 g (56%) of a viscous syrup came over at 164° (2 mm). After several days it crystallized; m. p. 115-117°.

Ethyl ester of 1,2,5-trimethyl-4-propionylaminopiperidyl-4-phosphonic acid (VII).   Prepared from 8.4 g (0.03 mole) of compound (I) in 90 ml of ligroine and 3 g (0.032 mole) of propionyl chloride in 6 ml of ligroine. 11 g (99%) of colorless crystals of the hydrochloride (VII) was obtained; decomp. temperature 99°. The compound is very hygroscopic, readily soluble in alcohol, acetone, chloroform; insoluble in ether and benzene.

Found %: P 8.3, 8.1; Cl 10.2, 10.1. $C_{15}H_{31}N_2PO_4 \cdot HCl$. Calculated %: P 8.3; Cl 9.6.

A solution of sodium ethoxide (0.72 g Na; 50 ml alcohol) was added to 11 g of hydrochloride (VII) in 10 ml of absolute alcohol. The precipitate was filtered off, the alcohol was distilled off, and the residue was distilled in vacuo. 5.4 g (53%) of a yellowish syrup came over at 109–111° ($3 \cdot 10^{-4}$ mm) and crystallized on standing. Recrystallization from ligroine gave colorless crystals with m. p. 105°.

Found %: C 53.7, 53.7; H 9.4, 9.3; N 8.2, 8.3; P 9.0, 9.2. $C_{15}H_{31}N_2PO_4$. Calculated %: C 53.9; H 9.4; N 8.4; P 9.3.

Ethyl ester of 1,2,5-trimethyl-4-benzoylaminopiperidyl-4-phosphonic acid (VIII).   10.3 g of hydrochloride (VIII) was prepared from 8.4 g (0.03 mole) of compound (I) in 90 ml of ligroine and 4.2 g (0.03 mole) of benzoyl chloride in 9 ml of ligroine; hygroscopic, yellowish substance with a decomposition point of 94°; it was dissolved in the minimum quantity of water and a saturated aqueous solution of sodium carbonate was added until the reaction was alkaline. The aqueous solution was extracted with benzene and the benzene extract was dried with sodium sulfate. The benzene was distilled off and the residue recrystallized from benzene.

4 g 35% colorless crystalline substance was obtained. M. p. 131–132°.

Found %: C 59.3, 59.2; H 8.2, 8.1; N 7.0, 7.0; P 7.9, 7.8. $C_{19}H_{31}N_2PO_4$. Calculated %: C 59.7; H 8.2; N 7.3; P 8.1.

Ethyl ester of 2,2-dimethyl-4-propionylaminotetrahydropyran-4-phosphonic acid (IX).   0.9 g (0.01 mole) of propionyl chloride was stirred into a mixture of 2.2 g (0.008 mole) compound (II), 0.8 g (0.01 mole) pyridine and 15 ml of benzene. The mixture was heated for 30 min at 50–60°. After cooling, the precipitate of pyridine hydrochloride was filtered off and the solvent was distilled off from the filtrate. The residue was recrystallized from a small quantity of ether. A second recrystallization gave 1.1 g (41%) of colorless substance with m. p. 97°.

Found %: C 52.5, 52.3; H 8.8, 9.0; N 4.1, 4.2; P 9.5, 9.7. $C_{11}H_{24}NPO_4$. Calculated %: C 52.3; H 8.8; N 4.4; P 9.6.

Ethyl ester of 1,2,5-trimethyl-4-hydroxypiperidyl-4-phosphoric acid (X).   Sodium ethoxide was stirred dropwise into a mixture of 7.05 g (0.05 mole) of 1,2,5-trimethyl-4-piperidone and 7 g (0.05 mole) of diethylphosphite. The temperature of the reaction mixture rose to 70°. The mixture was then heated for 30 min on a boiling water bath. From the reaction mixture a light fraction [36–50° (2 mm)] was drawn off. The rest was recrystallized from ethyl ether to give 4.5 g (32%) m.p. 82–83°.

Found %: C 51.6, 51.6; H 9.4, 9.5; N 4.9, 5.0; P 11.4, 11.2. $C_{12}H_{26}NPO_4$. Calculated %: C 51.6; H 9.4; N 5.0; P 11.1.

Ethyl ester of 2,2-dimethyl-4-hydroxytetrahydropyran-4-phosphonic acid (XI).   Sodium methoxide was stirred dropwise into a mixture of 12.8 g (0.1 mole) of 2,2-dimethyltetrahydropyran-4-one and 13.8 g (0.1 mole) of diethyl phosphite. The temperature of the reaction mixture rose to 80° during this operation. The mixture was then heated for 30 min on a boiling water bath. Crystals came down on the next day and were filtered and recrystallized from ligroine to give 15 g (56%) of a colorless substance with m.p. 75–76°.

Found %: C 49.3, 49.1; H 8.6, 8.6; P 11.7, 11.4. $C_{11}H_{23}PO_5$. Calculated %: C 49.6; H 8.7; P 11.6.

SUMMARY

1. It was shown that the previously discovered reaction of formation of aminoalkylphosphonic acids by the action of ammonia on a mixture of dialkyl phosphite and an aldehyde or ketone can be extended to heterocylic ketones.

2. Esters of aminophosphonic acids of the piperidine and tetrahydropyran series and some of their derivatives were prepared.

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BIS-(TRIALKYLSILYL) PHOSPHONATES

M. G. Voronkov, V. A. Kolesova, and V. N. Zgonnik

Trialkylsilyl esters of orthophosphoric acid $(R_3SiO)_n P(=O)(OH)_{3-n}$ (where n = 1-3) have often been described in the literature [1-4]. On the other hand, analogous derivatives of phosphorous acid $(R_3SiO)_n P(OH)_{3-n}$ were hitherto unknown. We made an attempt to synthesize tris-(trialkylsilyl) phosphites $(R_3SiO)_3P$ by reaction of trialkylmethoxysilanes with phosphorous acid according to the equation* :

$$3R_3SiOCH_3 + P(OH)_3 \rightarrow 3CH_3OH + (R_3SiO)_3P.$$
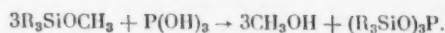
It was found, however, that even with a 4 : 1 molar ratio of reactants only bis-(trialkylsilyl) esters of phosphorous acid are formed:

$$2R_3SiOCH_3 + P(OH)_3 \rightarrow 2CH_3OH + (R_3SiO)_2POH,$$
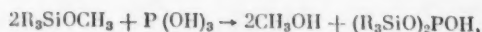
the yields of which are 50-70% of the theoretical (Table 1). In the reaction with trialkylalkoxysilanes, phosphorous acid consequently differs from phosphoric acid in substituting only two hydrogen atoms at the R_3Si group. This is

TABLE 1

Properties of Bis-(trialkylsilyl) Phosphonates

$[R_3SiO]_2P\langle^O_H$	B. p. in °C (p in mm Hg)		d_4^{20}	n_D^{20}	Found in %		Calc. in %		Yield in %
					P	Si	P	Si	
$[(CH_3)_3SiO]_2P\langle^O_H$	196 74—75	(763) (3)	0.9661	1.4145	14.11 14.45		13.68	24.82	57*
$[CH_3(C_2H_5)_2SiO]_2P\langle^O_H$	138—145	(6)	0.9498	1.4299	10.61 10.60		10.96	19.89	40**
$[(C_2H_5)_3SiO]_2P\langle^O_H$	152—153	(3)	0.9584	1.4402	9.88 9.82	18.1 18.3	9.97	18.09	67**
$[(C_3H_5)_3SiO]_2P\langle^O_H$	162—164	(5)		1.4412	10.18 10.22		9.97	18.09	73*
$[CH_3(n-C_3H_7)_2SiO]_2P\langle^O_H$	185—186	(17)	0.9373	1.4385	8.95 8.66	16.5 16.3	9.15	16.59	50**

* From R_3SiCl.

** From R_3SiOCH_3.

entirely typical since it was established [5] that phosphorous acid functions only as a dibasic acid corresponding

to the formula $(OH)_2P\langle^O_H$. In harmony with this fact, the dialkyl phosphites possess the analogous structure

$(RO)_2P\langle^O_H$ [5-11].

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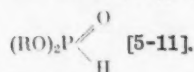
* We successfully performed a similar reaction for synthesis of tris-(trialkylsilyl) phosphates, bis-(trialkylsilyl) sulfates and tris-(trialkylsilyl) borates.

TABLE 2

Raman Spectra of Trialkylsilyl Esters of Phosphorous and Phosphoric Acids in cm^{-1}

$[(CH_3)_3SiO]_3P{-}O$	$[(CH_3)_3SiO]_2P(=O)H$	$[(C_2H_5)_3SiO]_2P(=O)H$	$[CH_3(C_4H_7)_2SiO]_2P(=O)H$	
170 (10)	171 (8)		173	
190 (5)	198 (10) bd		196	
220 (1) d	229 (1)		232 } (2)	
246 (4)	262 (7) bd	254 (1) d	265	
258 (5)	286 (1) d	303 (3)		
330 (1) ?	321 (0) bd			
345 (1) d	367 (1) bd	393 (0) d	351 (1) b	
	439 (0) bd		436 (0) d	
460 (1) d	507 (0) d			
	521 (1) d		520 (0) bd	
	566 (3) d	564 (10)d		
589 (7)	593 (8)		591 (1) bd	ν Si—C
614 (10)	610 (8)	623 (2) d	644 (1) d	ν Si—O
652 (5)	656 (10)	671 (0) d		
697 (7)	700 (10)	733 (2)	700 (1) d	ν P—O
760 (5)	765 (8)	753 (2) d	753 (2)	
846 (5) d	851 (6) bd		800 (2) d	
			873 (1)	
			897 (6)	δ H—P—O and ν C—C
	930 (0)	973 (8)		
	991 (3)	1008 (5)		
	1006 (3)	1018 (5)		
	1039 (1)		1032 (7)	
			1069 (5)	
	1093 (1)	1110 (1)	1103 (1)	ν P—O
1200 (1) d	1134 (4)		1206 (5) d	
1257 (5)	1259 (10) b	1232 (4)	1259 (2) d	ν P=O, δ CH
1275 (2)		1267 (1)		
1320 (1)	1322 (2)		1300 (3)	
			1341 (0) d	
1372 (1) ?	1383 (1)	1382 (1)d		δ CH
1414 (7)	1416 (10)	1412	1410 (8)	
		1465 (10)	1474 (10)	
	2426 (3) b	2423 (3) d	2429 (2) d	ν P—H
		2741 (1)	2735 (1) d	
	2887 (12)	2884 (12)	2874 (12)	ν C—H
2907 (10)		2917 (7)	2911 (12)	
		2942 (2)	2935 (3)	
2970 (10)	2970 (12)	2965 (10)	2968 (12)	

* d = diffuse, bd = broad diffuse, b = broad.

Examination of the Raman spectra of the bis-(trialkylsilyl) esters of phosphorous acid that we synthesized (Table 2) showed that they also possess the structure of bis-(trialkylsilyl) phosphonates $(R_3SiO)_2P(=O)H$.

The spectrum of these compounds contains the frequency of ~ 2425 cm^{-1} corresponding to the valence vibration of the P—H bond [6-10]. At the same time the characteristic frequency of the valence vibration of the P—O—H bond, lying in the 2550-2700 cm^{-1} region [7-10], is absent from all of the spectra that we studied. The vibration frequency of P=O appears in the 1260 cm^{-1} region in the spectra of bis-(trialkylsilyl) esters of phosphorous acid in agreement with the literature [6-10, 12]. The same spectral contains the frequencies of the deformation vibrations of H—C—H. In the spectrum of tris-(trimethylsilyl) phosphate $[(CH_3)_3SiO]_3P=O$ [2] (Table 2), which was plotted

for comparison, the vibration frequency of P=O is 1275 cm^{-1} – the same as in the infrared absorption spectrum of this compound that we measured.

The spectrum of bis-(trialkylsilyl) esters of phosphorous acid contain a series of frequencies in the 850-1050 cm^{-1} region which include the deformation frequencies of H–P–O [6-10]. The same region, however, also contains the C–C valence vibration. The frequency of about 850 cm^{-1}, characteristic of trimethyl phosphate (CH$_3$O)$_3$P=O but absent from the spectrum of triethyl phosphate [10], was observed by us only in the spectra of [(CH$_3$)$_3$SiO]$_3$P=O

and $[(CH_3)_3 SiO]_2 P \overset{\diagup O}{\underset{H}{\diagdown}}$. The frequencies of the symmetrical and antisymmetrical vibrations of the P–O

bond lie in the 700-760 cm^{-1} and 1090-1200 cm^{-1} regions, respectively [6-10, 12]. In the majority of cases a very weak band represents the frequency of the antisymmetrical vibration of P–O in the spectra of bis-(trialkyl-

silyl) phosphonates. Two lines are observed in the spectra of $[(CH_3)_3SiO]_2 P \overset{\diagup O}{\underset{H}{\diagdown}}$ and $[CH_3(C_3H_7)_2SiO]_2P \overset{\diagup O}{\underset{H}{\diagdown}}$

in this region. A tentative interpretation of all of the remaining frequencies in the spectra of trialkylsilyl esters of phosphorous and phosphoric acids is given in Table 2.

It is necessary to note that the synthesis of trialkylsilyl esters of phosphorous acid must be carried out in the absence of air and preferably in a nitrogen atmosphere. If this condition is not satisfied, the corresponding esters of orthophorphoric acid are also formed, frequently as the main product. Thus, for example, simple refluxing in an air stream of triethylmethoxysilane with phosphorous acid leads to tris-(triethylsilyl) phosphate (yield 54%).

Apart from the above method of synthesis of bis-(trialkylsilyl) phosphonates, the latter can be obtained by heating H$_3$PO$_3$ with trialkylchlorosilanes (in absence of air) according to the equation

$$2R_3SiC_l + (HO)_2 P \overset{\diagup O}{\underset{H}{\diagdown}} \rightarrow (R_3SiO)_2P \overset{\diagup O}{\underset{H}{\diagdown}} + 2HCl.$$
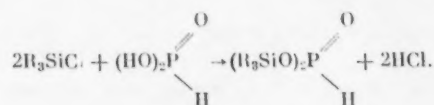
In this manner we prepared bis-(trimethylsilyl) and bis-(triethylsilyl) phosphonates in yields of 57 and 73% of the theoretical, respectively.

Bis-(trialkylsilyl) esters of phosphorous acid, whose physical properties, analytical data and yields are given in Table 1, are colorless liquids with a faint odor reminiscent of that of tris-(trialkylsilyl) phosphates; they are hydrolyzed by water (and also decomposed by alcohols) with formation of phosphorous acid; this behavior is the basis of our method of quantitative determination. Bis-(trialkylsilyl) esters of phosphorous acid do not give products of addition to cuprous chloride, which fact supports their structure as bis-(trialkylsilyl) phosphonates; they react with methyl magnesium iodide with liberation of methane, and the reaction is precisely quantitative in the

case of $[(C_2H_5)_3SiO]_2P \overset{\diagup O}{\underset{H}{\diagdown}}$. In the case of the three other esters as well as of diethyl phosphite, the yield

of methane is less than theoretical. It is interesting to note the extremely high thermal and chemical stability (toward , for example, HCl) of bis-(trialkylsilyl) phosphonates in comparison with their organic analogs

$(R_3CO)_2P \overset{\diagup O}{\underset{H}{\diagdown}}$ [13].
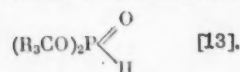
EXPERIMENTAL

Starting reactants. Trialkylmethoxysilanes were synthesized by reaction of the corresponding trialkylsilanes with CH$_3$OH in presence of sodium methoxide [14]. Trialkylchlorosilanes were prepared by reaction of hexaalkyl-disiloxanes with aluminum chloride [15]. All of the starting reactants were purified by distillation from a column with an efficiency of 15 theoretical plates, and they boiled to within 0.5°. Crystalline phosphorous acid was prepared by hydrolysis of PCl$_3$ [16] and was stored in a desiccator over sulfuric acid.

Analysis. Phosphorus and trialkylsilyl esters of phosphorous acid were determined as H_3PO_3 which is formed on their hydrolysis in an aqueous dioxan medium. The free acid was titrated as a monobasic acid with 0.2 N NaOH (indicator bromophenol blue). The Raman spectra were photographed on an ISP-51 spectrograph.

Synthesis of bis-(triethylsilyl) phosphonate. 28.3 g (0.193 mole) of triethylmethoxysilane was slowly distilled over 5.2 g (0.063 mole) of phosphorous acid. At 63-66°, 4.0 g (0.125 mole) of methyl alcohol distilled off; this was substantially the theoretical quantity.

Fractional distillation of the residue in vacuo gave 13.1 g (67%) of bis-(triethylsilyl) phosphonate with b. p. 146-153° (4 mm); after redistillation it had the constants listed in Table 1. Increase of the molar ratio of the starting components to 4 : 1 did not lead to appreciable increase in yield. Similarly the appropriate trialkylmethoxy-silanes gave

$$[CH_3(C_2H_5)_2SiO]_2P\overset{O}{\underset{H}{<}} \text{ and } [CH_3(C_3H_7)_2SiO]_2P\overset{O}{\underset{H}{<}}$$
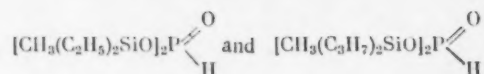
Synthesis of bis-(trimethylsilyl) phosphonate. 48.9 g (0.45 mole) of trimethylchlorosilane, 12.3 g (0.15 mole) of H_3PO_3 and 25 ml of benzene were refluxed until HCl ceased to come off. Fractional distillation of the reaction mixture gave 18.0 g (57%) of bis-(trimethylsilyl) phosphonate with b. p. 74-75°; n_D^{20} 1.4145 (Table 1). Similarly triethylchlorosilane gave bis-(triethylsilyl) phosphonate in 73% yield.

Reaction of triethylmethoxysilane with H_3PO_3 in an air stream. 32.2 g (0.22 mole) of triethylmethoxysilane and 5.7 g (0.07 mole) of phosphorous acid were refluxed in a current of dry air for 8 hrs. Fractional distillation then gave 5.4 g (80%) of methyl alcohol with b. p. 64-66° and 17.7 g (58%) of tris-(triethylsilyl) phosphate with b. p. 200-229° (12 mm); on redistillation it had b. p. 208° (10 mm); d_4^{20} 0.9668; n_D^{20} 1.4452.

Found %: P 7.02, 7.25. $C_{18}H_{45}O_4PSi_3$. Calculated %: P 7.03.

Reaction of H_3PO_3 with trimethylethoxysilane under similar conditions gave tris-(trimethylsilyl) phosphate with b. p. 98-104° (6 mm); n_D^{20} 1.4082.

Found %: P 9.91, 10.00. $C_9H_{27}O_4PSi_3$. Calculated %: P 9.85.

The Raman spectrum of this product was fully identical with that of $[(CH_3)_3SiO]_3P=O$ prepared by reaction of trimethylchlorosilane with H_3PO_4 or of hexamethyldisiloxane with P_2O_5 [2].

SUMMARY

Methods of synthesis of the previously unknown bis-(trialkylsilyl) phosphonates were developed on the basis of reaction of phosphorous acid with trialkylchlorosilanes or trialkylalkoxysilanes. Their Raman spectra were studied.

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SYNTHESIS OF SOME TRIPHENYLMETHYL- AND TRIPHENYLETHYLSILOXANES

V. S. Chugunov

We showed earlier [1, 2] that sodium triphenylsilanolate smoothly reacts with silicon tetrachloride and silicochloroform to form the corresponding triphenylchlorodisiloxanes or bis-(triphenylsiloxy)- and tris-(triphenylsiloxy) silanes. In the further course of these investigations it seemed of interest to carry out the reaction of sodium triphenylsilanolate in a benzene medium with some methyl- and ethylchlorosilanes. In this manner the synthesis was effected for the first time of triphenylalkylchlorodisiloxanes which distil at high temperatures without decomposition. Due to the presence of a labile chlorine or hydrogen at the silicon atom, these compounds can serve as starting substances for various high-molecular oxygen-containing organosilicon compounds. In addition, we also synthesized some crystalline methyl- and ethyl(triphenylsiloxy) silanes containing a branched Si—O—Si chain.

The composition and physicochemical constants of the compounds obtained are shown in the table.

EXPERIMENTAL

Triphenylmethyldichlorodisiloxane $(C_6H_5)_3SiOSiCH_3Cl_2$. 27.6 g of triphenylsilanol in 400 ml of dry benzene and 4 g of metallic sodium were placed in a round-bottomed flask protected against entry of moisture, and the contents were boiled for 4 hrs. After removal of the excess of unreacted sodium, 25 g of methyltrichlorosilane in 100 ml of benzene was added to the benzene solution (cooled with iced water) of sodium triphenylsilanolate, and the mixture was again boiled for 2 hrs. After separation of the sodium chloride, the solution was fractionally distilled to give 28.5 g of transparent, oily liquid which came over without decomposition.

Triphenylmethylchlorodisiloxane $(C_6H_5)_3SiOSiHCH_3Cl$. Into a benzene solution of sodium triphenylsilanolate (similarly prepared from 27.6 g of triphenylsilanol) was run 20 g of methyldichlorosilane in 100 ml benzene, and the mixture was boiled for 2 hrs. After separation of the sodium chloride and fractional distillation, 18.2 g of product was isolated as a colorless oil.

Bis-(triphenylsiloxy) methylsilane $[(C_6H_5)_3SiO]_2SiHCH_3$. To sodium triphenylsilanolate, prepared from 10.8 g of triphenylsilanol in 200 ml benzene, was added at room temperature 12 g of methyldichlorosilane in 50 ml of benzene, and the mixture was boiled for 3 hrs. After elimination of sodium chloride, the solution was evaporated in vacuo to one-third of its original volume. The crystals were recrystallized from benzene. 20.1 g (42.5% yield calculated on the methyldichlorosilane) of crystalline bis-(triphenylsiloxy)methylsilane was obtained.

Bis-(triphenylsiloxy)dimethylsilane $[(C_6H_5)_3SiO]_2Si(CH_3)_2$. To a solution of sodium triphenylsilanolate, prepared from 13.8 g of triphenylsilanol in 200 ml benzene, was added (with cooling to 0°) 6 g of dimethyldichlorosilane, and the mixture was boiled for 3 hrs. After separation of the sodium chloride, the filtrate was evaporated to one-half its volume. The resultant crystals were recrystallized from benzene to give 7.6 g of finely crystalline bis-(triphenylsiloxy) dimethylsilane.

Tris-(triphenylsiloxy) methylsilane $[(C_6H_5)_3SiO]_3SiCH_3$. Sodium triphenylsilanolate was prepared from 11.5 g of triphenylsilanol in 200 ml benzene. Addition was then made to the solution at room temperature of 7.8 g of methyltrichlorosilane in 50 ml of benzene, and the mixture was boiled for 3 hrs. The resultant crystals were twice recrystallized from benzene to give 3.7 g of finely crystalline product.

TABLE

Serial no.	Formula of compound	M. p. in °C	B. p. in °C	d_4^{20}	n_D^{20}	MR found	MR calc.	Cl content in % found	Cl content in % calc.	Si content in % found	Si content in % calc.	Yield in %
1	$(C_6H_5)_3SiOSiCH_3Cl_2$	—	368—372	1.2060	1.575	106.72	107.64	17.9 / 18.0	18.2	14.0 / 14.1	14.4	71
2	$(C_6H_5)_3SiOSiHCH_3Cl$	—	356—362	1.1182	1.567	103.73	103.64	9.8 / 9.9	10.0	15.5 / 15.6	15.8	64.6
3	$[(C_6H_5)_3SiO]_2SiHCH_3$	170—171	—	—	—	—	—	—	—	13.9 / 14.0	14.1	42.5
4	$[(C_6H_5)_3SiO]_2Si(CH_3)_2$	155—156	—	—	—	—	—	—	—	13.2 / 13.4	13.8	49.8
5	$[(C_6H_5)_3SiO]_3SiCH_3$	224—225	—	—	—	—	—	—	—	12.3 / 12.5	12.9	34.5
6	$(C_6H_5)_3SiOSiC_2H_5Cl_2$	—	370—376	1.1618	1.572	113.68	112.27	17.2 / 17.3	17.6	13.4 / 13.6	13.9	69.5
7	$(C_6H_5)_3SiOSiHC_2H_5Cl$	—	365—370	1.1132	1.568	108.44	108.27	9.3 / 9.5	9.6	15.2 / 15.0	15.2	58.4
8	$[(C_6H_5)_3SiO]_3SiC_2H_5$	219—220	—	—	—	—	—	—	—	12.1 / 12.3	12.7	26.0

Triphenylethyldichlorodisiloxane $(C_6H_5)_3SiOSi \cdot C_2H_5Cl_2$. To a solution of sodium triphenylsilanolate, prepared from 27.6 g of triphenylsilanol in 400 ml of benzene, was added 30 ml of ethyltrichlorosilane in 100 ml of benzene. After boiling for 3 hrs and separation of the sodium chloride, the filtrate was fractionally distilled to give 28 g of product which came over without decomposition in the form of an oily liquid.

Triphenylethylchlorodisiloxane $(C_6H_5)_3SiOSiHC_2H_5Cl$. Sodium triphenylsilanolate was prepared from 27.6 g of triphenylsilanol in 400 ml of benzene. 25 g of ethyldichlorosilane was added, and the mixture was boiled for 3 hrs. Fractional distillation of the filtrate gave 21.5 g of product.

Tris-(triphenylsiloxy) ethylsilane $[(C_6H_4)_3SiO]_3 \cdot SiC_2H_5$. Sodium triphenylsilanolate was prepared from 13.8 g of triphenylsilanol in 200 ml of benzene. 10 g of ethyltrichlorosilane in 50 ml of benzene was then run in at room temperature, and the mixture was boiled for 3 hrs. After separation of the sodium chloride, a large proportion of the benzene was removed in vacuo. The remaining crystals were twice recrystallized from benzene to give 5.7 g of product which melted without decomposition.

SUMMARY

For the first time 8 pure oxygen-containing organosilicon compounds were prepared; some of them can be utilized for the preparation of high-molecular organosilicon polymers.

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THE CURTIUS REARRANGEMENT OF ISOMERIC CYCLOHEPTATRIENECARBOXYLIC AND NORCARADIENECARBOXYLIC ACIDS

D. N. Kursanov, M. E. Volpin, I. S. Akhrem, and I. Ya. Kachkurova

In 1954 a communication [1] appeared on the preparation of cycloheptatrienylium (tropylium) salts:


Tropylium is a stable, seven-membered carbonium ion possessing aromatic properties. Considerable interest is attached to a study of the possible routes of formation of the tropylium ion from cycloheptatriene and its derivatives. Dewar and Pettit recently reported [2] that the Curtius rearrangement of a mixture of azides of β-cycloheptatrienecarboxylic and norcaradienecarboxylic acids is accompanied by isomerization of the migrating radical and by formation of a tropylium ion salt according to the equation: $C_7H_7-CON_3 \rightarrow (C_7H_7)^+ + NCO^- + N_2$. On the other hand, Johnson, Langemann and Tisler [3] reported that no tropylium salt at all was formed on carrying out the Curtius rearrangement of the azide of α-cycloheptatrienecarboxylic acid, although the formation of the tropylium system is actually more probable when starting from the α-cycloheptatrienyl radical. Unfortunately the latter paper does not establish whether the structure of the migrating cycloheptatrienyl radical is retained and whether it isomerizes with double-bond shift. In view of the conflicting literature data and the importance of a solution of this problem both for the chemistry of the new aromatic tropylium system and for the understanding of the mechanism of the Curtius rearrangement, it was necessary to investigate it more closely.

In the present work we made a systematic study of the Curtius rearrangement in the series of isomeric α-cycloheptatrienecarboxylic (I) (R = COOH), β-cycloheptatrienecarboxylic (II) (R = COOH), γ-cycloheptatrienecarboxylic (III) (R= COOH) and norcaradienecarboxylic (IV) (R = COOH) acids.*

(I)	(II)	(III)	(IV)
(α-series)	(β-series)	(γ-series)	(hor-series)
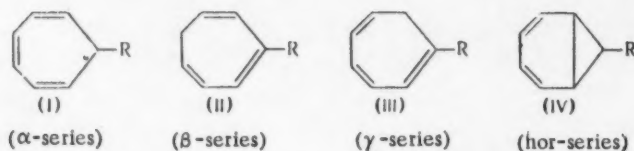
Rearrangement proceeds according to an equation of the general form:

$$C_7H_7-C\overset{O}{\underset{N_3}{\diagdown}} \rightarrow C_7H_7-N=C=O + N_2.$$

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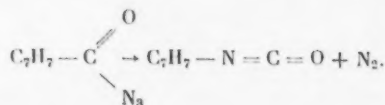
* The designations of α-, β-, and γ- are the arbitrary ones accepted in the literature.
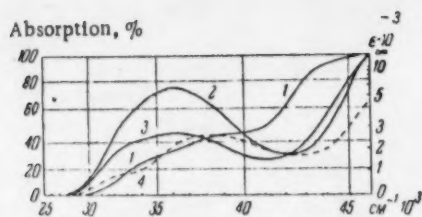
Fig. 1. Absorption spectra: 1) α-, 2) β-, and 3) γ-cycloheptatrienecarboxylic acids; 4) norcaradiene-carboxylic acid (isooctane as solvent, concentration $1 \cdot 10^{-3}$ M).
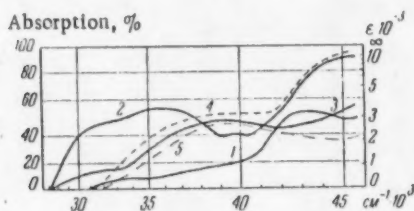

Fig. 2. Absorption spectra of acid chlorides: 1) α-, 2) γ-cycloheptatrienecarboxylic acids; 3) norcara-dienecarboxylic acid (dense curves). Spectra of amides: 4) α-cycloheptatrienecarboxylic acid and 5) norcaradienecarboxylic acid (isooctane as solvent for acid chlorides; ethanol as solvent for amides; concentration $1 \cdot 10^{-3}$ M).

It is known [4] that the α- and β-nor systems (I) and (IV) readily isomerize with formation of the more stable β-system (II), which in turn is capable of rearranging to the γ-system (III) with a longer conjugated chain. Special attention is consequently given not only to the question of formation of a tropylium salt during rearrangement but also to the question of whether α-cycloheptatrienyl and norcaradienyl radicals isomerize to derivatives of the β- and γ-series. With this objective, we studied the absorption spectra of the prepared compounds in the ultraviolet region (25,000 to 50,000 cm^{-1}).

Starting substances for the azides were pure α-, β-, and γ-cycloheptatrienecarboxylic and norcaradiene-carboxylic acids. The corresponding acid chlorides were obtained from the four acids by the action of thionyl chloride. The chlorides are represented by formulas (I to IV) above where R = COCl. Reaction of the latter with NaN$_3$ gave the azides of (I – IV) (R = = CON$_3$). In addition to the amides of α-cyclohepta-trienecarboxylic (I) (R = CONH$_2$) and norcaradienecar-boxylic (IV) (R = CONH$_2$) acids were prepared.

The absorption spectra of the starting cyclohepta-trienecarboxylic acids (Fig. 1, table) agree in the main with the spectra described by Grundmann and Ottmann [4] and confirm the structure of these acids. The occurrence in the β- and γ-acids of conjugation of the carboxyl with two or three double bonds is reflected in the appreciable shift of the maxima of absorption into the long-wave region in comparison with unsubstituted cyclo-

heptatriene (ν_{max} 37,000-38,000 cm^{-1}, ϵ_{max} 4.4 $\cdot 10^3$) [5]. The marked difference in the spectra of α-cyclo-heptatrienecarboxylic acid (I) (R = COOH) and its derivatives enable facile detection of compounds of the α-series and their isomers. As we see from Fig. 2 and the table, the spectra of the acid chlorides and the amides, as well as that of the azide of (I) (R = CON$_3$) in the main retain their character of the spectra of the corresponding acids, thus confirming the absence of isomerization during their preparation.

Particular interest is attached to the spectrum of norcaradienecarboxylic acid (IV) (R = COOH), which was similar to the spectra of β- and γ-cycloheptatrienecarboxylic acids and different from the spectrum of the α-acid (Fig. 1). The presence of an absorption maximum at 38,500-39,000 cm^{-1} for the nor-acid can be explained by transfer of the conjugation of the three-membered ring which leads to formation of a continuous chain of conjugation with participation of the C=O of the carboxyl group and the double bonds of the ring. This explanation is supported by the data of Eastman and Freeman [6] who showed that in disubstituted cyclopropanes the three-membered ring possesses chromophoric properties in the same way as the vinyl group if it is located between two chromophores. In our case all of the three substituents in the three-membered ring are chromophores. The theory of the conjugation of the three-membered ring with double bonds is also supported by other spectroscopic data [7] as well as by the dipole moments [8] and the reactions [9] of cyclopropane derivatives.

When the azides of α-, β-, and γ-cycloheptatrienecarboxylic acids (I – III) (R = CON$_3$) and of norcaradiene-carboxylic acid (IV) (R = CON$_3$) were subjected to the Curtius rearrangement by heating in benzene, it was found that in all cases only the covalent isocyanates were formed (in satisfactory yields); the latter are liquids which are in-soluble in water and soluble in benzene, ether and other nonpolar solvents; they give the reactions characteristic of ordinary isocyanates. In no case was the formation of a benzene-insoluble ionic tropylium salt observed. Co-valent isocyanates alone were similarly obtained when the transformation was carried out on a mixture of β-cyclo-heptatrienecarboxylic acid and norcaradienecarboxylic acid prepared by the method of Dewar and Pettit [2], as

TABLE

Absorption Spectra in the Ultraviolet of Derivatives of Cycloheptatriene and Norcaradiene

Substituent R	System			
	(I) (α-series)	(II) (β-series)	(III) (γ-series)	(IV) (nor-series)
—COOH*	Flat curve, no maximum	$\nu_{max} = 36\ 000$ см$^{-1}$ $\varepsilon_{max} = 5.7 \cdot 10^3$	$\nu_{max} = 36\ 300$ $\varepsilon_{max} = 2.7 \cdot 10^3$	$\nu_{max} = 38\ 500$ $\varepsilon_{max} = 2.6 \cdot 10^3$
—COCl*	No maximum		$\nu_{max} = 35\ 500$ см$^{-1}$ $\varepsilon_{max} = 3.5 \cdot 10^3$	$\nu_{max} = 39\ 000$ см$^{-1}$ $\varepsilon_{max} = 2.8 \cdot 10^3$
—CONH$_2$**	$\nu_{max} = 39\ 000 - 40\ 000$ см$^{-1}$ $\varepsilon_{max} = 2.7 \cdot 10^2$	—	—	$\nu_{max} = 39\ 000$ см$^{-1}$ $\varepsilon_{max} = 2.9 \cdot 10^3$
—CON$_3$*	No maximum	—	—	—
—NCO*	$\nu_{max} = 38\ 000$ см$^{-1}$ $\varepsilon_{max} = 3.2 \cdot 10^3$	$\nu_{max} = 37\ 000$ см$^{-1}$ $\varepsilon_{max} = 4.8 \cdot 10^2$	$\nu_{max} = 36\ 000$ см$^{-1}$ $\varepsilon_{max} = 3.0 \cdot 10^3$	$\nu_{max} = 36\ 000$ см$^{-1}$ $\varepsilon_{max} = 3.2 \cdot 10^3$
—NHCONH$_2$**	$\nu_{max} = 37\ 700$ см$^{-1}$ $\varepsilon_{max} = 2.4 \cdot 10^3$	$\nu_{max} = 36\ 500$ см$^{-1}$ $\varepsilon_{max} = 7.3 \cdot 10^3$	$\nu_{max} = 34\ 000$ см$^{-1}$ $\varepsilon_{max} = 5.6 \cdot 10^3$	$\nu_{max} = 38\ 000$ см$^{-1}$ $\varepsilon_{max} = 0.8 \cdot 10^3$
—NHCONHC$_6$H$_5$**	$\nu_{max} = 40\ 000$ см$^{-1}$ $\varepsilon_{max} = 2.5 \cdot 10^3$	$\nu'_{max} = 36\ 000$ см$^{-1}$ $\varepsilon'_{max} = 15 \cdot 10^3$ $\nu''_{max} = 40\ 500$ см$^{-1}$ $\varepsilon''_{max} = 23 \cdot 10^3$	$\nu'_{max} = 32\ 000 - 35\ 000$ см$^{-1}$ $\varepsilon'_{max} = 8 \cdot 10^3$ $\nu''_{max} = 40\ 500$ см$^{-1}$ $\varepsilon''_{max} = 19 \cdot 10^3$	$\nu'_{max} = 33\ 000$ см$^{-1}$ $\varepsilon'_{max} = 13 \cdot 10^3$ $\nu''_{max} = 41\ 000$ см$^{-1}$ $\varepsilon''_{max} = 22 \cdot 10^3$

* Isooctane as solvent.

** Ethyl alcohol as solvent.
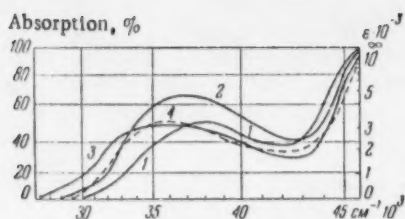
Fig. 3. Absorption spectra: 1) α-, 2) β-, and 3) γ-cycloheptatrienly isocyanates; 4) norcaradienyl isocyanate (isooctane as solvent).

Fig. 4. Absorption spectra: 1) α-, 2) β-, and 3) γ-cycloheptatrienyl ureas; 4) norcaradienyl urea (ethanol as solvent; concentration $1 \cdot 10^{-3}$ M).

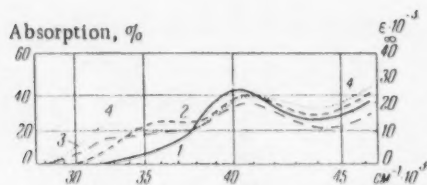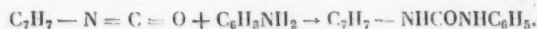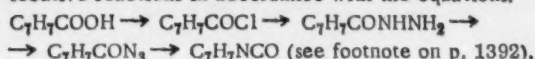Fig. 5. Absorption spectra: 1-3) N-phenyl-N', α-, β-, and γ-cycloheptatrienyl ureas and 4) N-phenyl-N'-norcaradienyl urea (ethanol as solvent; concentration $11 \cdot 10^{-4}$ M).

well as when the same mixture was subjected to consecutive reactions in accordance with the equations:
$C_7H_7COOH \rightarrow C_7H_7COCl \rightarrow C_7H_7CONHNH_2 \rightarrow$
$\rightarrow C_7H_7CON_3 \rightarrow C_7H_7NCO$ (see footnote on p. 1392).

The absorption spectra of the isocyanates (Fig. 3 and table) indicate that various compounds are formed during the rearrangement, and the character of the spectra and their resemblance to those of the corresponding acids (apart from the α-isocyanate) permit us to assume that the migrating radical does not isomerize during the Curtius rearrangement. The curve for α-cycloheptatrienyl isocyanate (I) (R = NCO) is similar to the curve of unsubstituted cycloheptatriene [5].

The absence of isomerism in the course of re-arrangement was more convincingly demonstrated by investigated of the urea derivatives obtained from the isocyanates by the action of urea:

$$C_7H_7 - N = C = O + NH_3 \rightarrow C_7H_7 - NHCONH_2$$
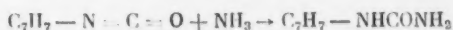
The resultant α-, β-, and γ-cycloheptatrienyl ureas (I - III) (R = NHCONH$_2$) and norcaradienyl urea (IV) (R = NHCONH$_2$) are nicely crystallizing and sharply melting substances; their mixtures in various combinations invariably exhibit a depression of melting point, thus demonstrating the nonidentity of the compounds. Further conclusive proof of the absence of isomerization is furnished by the adsorption spectra of these urea derivatives (Fig. 4); in the case of α-, β-, and γ-cycloheptatrienyl derivatives, the spectra retain all the characteristics of the original systems. It is remarkable that transition from isocyanate to urea derivative leads to a sharp change in the spectrum of the norcaradienyl derivative; absorption is lowered by a factor of 3-4; this is associated with the presence in the urea derivative in the radical R of a double bond conjugated with the three-membered ring.

Reaction of the isocyanates with aniline also gave the corresponding derivatives: N-phenyl-N'-cycloheptatrienyl urea (I - III) (R = NHCONHC$_6$H$_5$) and N-phenyl-N,-norcaradienyl urea (IV) (R = NHCONHC$_6$H$_5$):

$$C_7H_7 - N = C = O + C_6H_5NH_2 \rightarrow C_7H_7 - NHCONHC_6H_5.$$

Their absorption spectra (Fig. 5, table) possess an intensity greater by one order than the compounds considered above, and the character of their curves is different. Comparison with the spectra of phenylurea (λ_{max} 41,500 cm^{-1}, $\epsilon = 16 \cdot 10^3$) and diphenylurea (λ_{max} = 39,000 cm^{-1}, $\epsilon = 25 \cdot 10^3$) shows that the absorption maximum in the 39,000-42,000 cm^{-1} region is associated with the presence of the NHCONHC$_6$H$_5$ grouping. The absorption of the β- and γ-cycloheptatrienyl derivatives of phenylurea in the 30,000-37,000 cm^{-1} region corresponds to that for derivatives of urea (Fig. 4); in this region of frequencies a regular difference in relation to the spectrum of the α-cycloheptatrienyl derivative is observed. A striking feature is the development of an absorption maximum in the 33,000 cm^{-1} region in the spectrum of the norcaradienyl derivative of phenylurea (IV) (R = NHCONHC$_6$H$_5$).

Thus, the properties of the isocyanates, substituted ureas and phenylureas and their ultraviolet absorption spectra indicate the absence of isomerization, during the Curtius rearrangement, of the migrating 2,4,6-, 1,3,6-, and 1,3,5-cycloheptatrienyl radicals, and the norcaradienyl radical.

The results are consistent with data from a study of the Curtius rearrangement of optically active compounds [10]. Absence of racemization and retention of the configuration of the migrating radical was here observed in all cases. All these facts, together with the data of the present work, confirm the inner-molecular character of the Curtius rearrangement.*

EXPERIMENTAL

The starting ethyl esters of β-cycloheptatrienecarboxylic and norcaradienecarboxylic acids required for later syntheses were prepared by Buchner's method [12] — heating of benzene with ethyl diazoacetate (20 : 1) in ampoules at 135-136° for 5 hrs. The yield of fraction with b. p. 104-109° (12 mm) was 40%. Norcaradienecarboxylic acid was isolated from the mixture in the form of the amide [2], yield 27%, m. p. 140°. The literature reports 141° [2].

The acid chlorides, azides, isocyanates, ureas and phenylureas were prepared by similar methods from the corresponding acids in all cases. The preparation of these derivatives from α-cycloheptatrienecarboxylic acid is described below in more detail to illustrate the procedures. Only the yields and constants are given for the remaining substances that were prepared.

Derivatives of α-Cycloheptatrienecarboxylic Acid

α-Cycloheptatrienecarboxylic acid was obtained by saponification of the amide of norcaradienecarboxylic acid [4]; yield 70%. After recrystallization from water it had m. p. 71°; the literature reports 71° [4].

Acid chloride and amide of α-cycloheptatrienecarboxylic acid. A solution of 1.9 g of α-cycloheptatriene-carboxylic acid in 10 ml of thionyl chloride was boiled for 45-50 min. Removal of the thionyl chloride by distillation, followed by fractionation, gave 2.0 g of α-cycloheptatrienecarboxylic acid chloride; yield 93%, b. p. 87.5-91° (7 mm).

Passage of ammonia into an ethereal solution of the acid chloride gave α-cycloheptatrienecarboxylic acid amide; yield 75 %; m. p. 124°. Literature: m. p. 129° [13].

Azide of α-cycloheptatrienecarboxylic acid and 2,4,6-cycloheptatrienyl isocyanate. To a solution of 2 g of the acid chloride in 25 ml of acetone (cooled to 0°) was added a solution of 2 g of sodium azide in 2.5 ml of water. The ice-cooled reaction mixture was carefully stirred for 20-25 min. 50 ml of iced water was then added, and the precipitated oil was extracted with ether. The ethereal solution was twice washed with water and dried with magnesium sulfate. After the ether had been driven off, absolute benzene was added to the residue. The azide was decomposed by heating the benzene to the boil. After nitrogen had ceased to come off, the benzene was driven off, and the residue was distilled in vacuo to give 1.45 g of 2,4,6-cycloheptatrienyl isocyanate; yield 84%; b. p. 67° (6 mm); n_D^{20} 1.5455. The isocyanate is unstable in the air, and readily decomposes and polymerizes.

Found %: C 72.23, 71.54; H 5.49, 5.46. C_8H_7ON. Calculated %: C 72.16; H 5.30.

2,4,6-Cycloheptatrienyl urea. An ammonia stream was passed through a solution of 0.2010 g of isocyanate in 3 ml of absolute ether. The precipitate was filtered off. 0.1520 g of 2,4,6-cycloheptatrienyl urea was obtained; yield 68%. After recrystallization from absolute benzene it had m. p. 126-127°. Soluble in acetone, dioxan and alcohol; insoluble in benzene, isooctane and ether. A mixture of 2,4,6-cycloheptatrienyl urea (α-series) with 1,3,6-cycloheptatrienyl urea (γ-series) melts at 109°.

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* After the present paper had gone to press, Dewar and Pettit [11] published a paper in which the Curtius rearrangement was also studied in the α-, β-, and γ-cycloheptatrienecarboxylic acids and in norcaradienecarboxylic acid. They point out that, in addition to the covalent isocyanate, the azide of norcaradienecarboxylic acid under some conditions also forms tropylium isocyanate in a yield of 0 to 50%. Dewar and Pettit infer from the nontransformation of α-cycloheptatrienecarboxylic acid into a tropylium salt during the Curtius rearrangement that this acid has a structure different from that previously assigned to it.

Found %: C 63.35, 63.75; H 6.84, 6.57. $C_8H_{10}ON_2$. Calculated %: C 63.97; H 6.71.

N-Phenyl-N'-2,4,6-cycloheptatrienyl urea. An excess of aniline was added dropwise to a solution of 0.4003 g of isocyanate in 2.5 ml of absolute ether. The reaction went with appreciable liberation of heat; the phenylurea derivative came down; insoluble in ether, isooctane, benzene, cold alcohol and water. Yield 0.045 g (79%). After numerous recrystallizations from alcohol it melted at 185° (with much decomposition).

Found %: N 12.34, 12.55. $C_{14}H_{14}ON_2$. Calculated %: N 12.39.

Derivatives of β-Cycloheptatrienylcarboxylic Acid.

The starting ethyl ester of β-cycloheptatrienecarboxylic acid was obtained by heating a mixture of the ethyl esters of norcaradienecarboxylic and β-cycloheptatrienecarboxylic acids in vacuo at 150° for 6 hrs [4]; yield 89%; b. p. 121° (22 mm); 112.2-114.5° (15 mm). The literature reports b. p. 115° (15 mm) [14].

Alkaline saponification of this ester [4] gave β-cycloheptatrienecarboxylic acid; yield 70%; b. p. 151-155° (12 mm); m. p. 55-56°. Literature data: b. p. 151-154° (12 mm); m. p. 56° [4].

β-Cycloheptatrienecarboxylic acid chloride. 2.7 g β-cycloheptatrienecarboxylic acid gave 2.75 g of the acid chloride; yield 91.7%; b. p. 95-100° (9 mm); 87.5-88.5° (6 mm).

1,3,6-Cycloheptatrienyl isocyanate. 0.70 g of β-cycloheptatrienecarboxylic acid chloride gave 0.51 g of · isocyanate with b. p. 70.5-72° (10 mm); yield 84%.

Found %: C 72.17, 72.09; H 5.47, 5.41; N 10.82, 10.82. C_8H_7ON. Calculated %: C 72.16; H 5.30; N 10.52.

1,3,6-Cycloheptatrienyl urea. M.p. 131-132° after recrystallization from absolute benzene. A mixture of 1,3,6-cycloheptatrienyl urea (β-series) and 2,4,6-cycloheptatrienyl urea (α-series) melted at 109°. A mixture of norcaradienyl urea with 1,3,6-cycloheptatrienyl urea melted at 126°.

N-Phenyl-N'-1,3,6-cycloheptatrienyl urea. M. p. 184° (with decomposition) after recrystallization from absolute alcohol.

Found %: C 74.40, 74.13; H 6.46, 6.27; N 12.30, 12.18. $C_{14}H_{14}ON_2$. Calculated %: C 74.30; H 6.23; N 12.39.

Derivatives of γ-Cycloheptatrienecarboxylic Acid

γ-Cycloheptatrienecarboxylic acid was prepared by the method of Grundmann and Ottmann [4]; yield 47%; b. p. 143-145° (6 mm); n_D^{16} 1.5610. Literature data: b. p. 103-104° (0.6 mm); n_D^{26} 1.5670 [4].

γ-Cycloheptatrienecarboxylic acid chloride. 1.67 g of γ-cycloheptatrienecarboxylic acid gave 1.33 g of acid chloride; yield 70%; b. p. 79-85° (3 mm).

1,3,5-Cycloheptatrienyl isocyanate. 1.33 g of acid chloride gave 1.05 g of 1,3,5-cyclopentatrienyl isocyanate; yield 92%; b. p. 61° (6 mm).

1,3,5-Cycloheptatrienyl urea. M. p. 140° after two recrystallizations from absolute benzene. A mixture of 2,4,6-(α-series) and 1,3,5-cyclopentatrienyl (γ-series) ureas melted at 109°. A mixture of norcaradienyl urea and 1,3,5-cycloheptatrienyl urea melted at 115-118°.

Found %: C 63.94; H 6.68. $C_8H_{10}ON_2$. Calculated %: C 63.97; H 6.71.

N-phenyl-N'-1,3,5-cycloheptatrienyl urea has m. p. 183-184° (with much decomposition) after recrystallization from absolute alcohol. Derivatives of the γ-series are particularly unstable (they turn yellow on keeping in the air and the constants change).

Derivatives of Norcaradienecarboxylic Acid

Norcaradienecarboxylic acid was prepared by acid hydrolysis of its amide by the Buchner method [12]; yield 34%; b. p. 117° (3 mm).

Norcaradienecarboxylic acid chloride. 1.88 g of acid chloride was obtained from 1.90 g of acid; yield 87%; b. p. 85-90° (9 mm).

Norcaradienyl isocyanate. 1.21 g of isocyanate was prepared from 1.88 g of the acid chloride; yield 82%; b. p. 80-85° (13 mm).

Norcaradienyl urea. M. p. 145° after recrystallization from absolute benzene. A mixture of norcaradienyl urea with 1,3,5-cycloheptatrienyl urea (γ-series) melts at 115-118°. A mixture of norcaradienyl urea with 1,3,6-cycloheptatrienyl urea (β-series) melts at 126°.

Found %: C 63.94; H 6.80. $C_8H_{10}ON_2$. Calculated %: C 63.97; H 6.71.

N-Phenyl-N'-norcaradienyl urea has m. p. 184° (with much decomposition) after recrystallization from absolute alcohol.

The ultraviolet absorption spectra were measured with the SF-4 automatic spectrophotometer. This was fitted with the Palitsina high-speed photographic attachment. Apart from phenylurea derivatives the measurements were carried out at concentrations of $1 \cdot 10^{-3}$ M; the concentration of phenyl urea derivatives was $1 \cdot 10^{-4}$ M.

SUMMARY

1. The Curtius rearrangement in isomeric β- and γ-cycloheptatrienecarboxylic acids and norcaradiene-carboxylic acid was studied. It was shown that rearrangement goes without isomerization of the migrating hydrocarbon radical under the conditions employed.

2. The following were synthesized for the first time: 1,3,5-, 1,3,6- and 2,4,6-cycloheptatrienyl isocyanates, norcaradienyl isocyanates, 1,3,5-, 1,3,6- and 2,4,6-cycloheptatrienyl ureas, norcaradienyl urea, N-phenyl-N'-1,3,5-, -1,3,6-, and -2,4,6-cycloheptatrienyl ureas, and N-phenyl-N'-norcaradienyl urea.

3. The absorption spectra in the near ultraviolet (25,000-50,000 cm^{-1}) of 22 derivatives of cycloheptatriene and norcaradiene were examined. It was shown that in nocaradiene derivatives (IV, R = COOH, COCl, $CONH_2$, NCO) the three-membered ring transmits conjugation in a similar manner to a double bond.

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SYNTHESIS OF VINYL ESTERS OF ISOBUTRYIC, ISOVALERIC
AND CAPROIC ACIDS

E. N. Rostovsky, A. N. Barinova, and A. I. Volkova

In recent years vinyl esters have attracted the attention of investigators, especially in connection with the production from them of graft polymers [1] and with the properties of certain copolymers [2, 3]. Little attention has been given, however, to vinyl esters of different carboxylic acids apart from vinyl acetate. We synthesized some of these esters for the first time. Study of individual monomers of one and the same homologous series is of interest since their properties, as well as those of the derived polymers, can be varied considerably in dependence upon the structure.

Various reactions have been used by different investigators for the preparation of the esters: interaction of carboxylic acid with acetylene in the liquid phase (preferably under pressure) [2, 4-7], the vapor-phase heterogeneous catalytic method [8-10], acidolysis of vinyl acetate [11-14] or of vinyl ethers [15], or acylation of the enol form of acetaldehyde [16, 17]. According to the literature [4], the liquid-phase synthesis from acetylene in presence of mercury catalyst is applicable only to lower aliphatic acids, and this was confirmed in our experiments. Thus, for example, the interaction of acetylene with isobutyric acid under the conditions of the usual liquid-phase process at ordinary pressure (4% mercuric phosphate as a catalyst, reaction temperature 60-98°) goes very slowly, the yield of vinyl ester after 4 hrs being ~ 3%.

Under the same conditions acetylene combines very vigorously with acetic or formic acid. The low activity of isobutyric acid is evidently associated with the properties of the acetylene—catalyst complex (stability, solubility, etc.). Reppe prepared vinyl esters from acetylene and acids by employing elevated pressures and temperatures with zinc or cadmium salts as catalysts [4, 7]. Transesterification [acidolysis] of vinyl acetate with carboxylic acids in presence of mercury catalysts was first proposed by Toussaint and MacDowel [11] and was extensively applied in work cited above [12, 14].

Jointly with Ushakov and Arbuzova [8-10] we had previously studied the vapor-phase heterogeneous catalytic method of synthesis of vinyl acetate and some other vinyl esters. We had established that the thermal stability of the carboxylic acid, the formation of ethylidene esters and certain other secondary reactions limit the useful conversion of the acid in question to varying degrees.

We also arrived at the conclusion [10] that the mechanism of the liquid-phase reaction of acetylene with acids and the heterogeneous catalytic synthesis might be regarded from the same viewpoint (formation of a complex of acetylene with catalyst, its decomposition by the acid at a rate depending upon the temperature and other conditions). In the present work we examine the synthesis of vinyl esters of isobutyric, isovaleric and caproic acids by two methods: vapor-phase heterogeneous catalysis and acidolysis of vinyl acetate. We consider it is necessary to compare the latter reaction with liquid- and vapor-phase methods of preparation of vinyl esters since similar conditions are applicable to acidolysis, and the same mercury catalysts (as used for reaction of acetylene with acids) can be used. Moreover, we took into consideration the ideas of Adelman [12] on the mechanism of acidolysis of vinyl acetate. In his opinion, this reaction differs from transesterification and it involves dissociation of vinyl acetate in presence of catalyst to form acetic acid and a mercury-acetylene complex which in turn reacts with acids.

In experiments on syntheses with isobutyric, isovaleric and caproic acids, we were also able to establish the degree of development of secondary processes and the desirability of selecting one method or the other for the different acids. For this purpose we also studied the extent of straight addition of acid at the vinyl bond.

Zavgorodny's experiments [18] on reaction of some carboxylic acids with olefinic hydrocarbons showed that the structure of the acid and the solvent, apart from the nature of the catalyst, have a marked influence upon the kinetics of this reaction. On treating pseudobutylene with acetic acid in presence of catalyst (boron fluoride etherate with red oxide of mercury), Zavgorodny observed, for example, a maximum yield of ester; subsequent heating led to fall in yield of 1,2-dimethylethyl acetate.

EXPERIMENTAL

Synthesis of vinyl isobutyrate. Vapor-phase synthesis was effected in an apparatus similar to that previously described [8-10]; acetylene from a cylinder, after further purification and drying, was passed into a glass vaporizer heated by an ultrathermostat. The acetylene/acid ratio was regulated through the temperature of the vapor in front of the catalytic apparatus, and in the experiments described below it was approximately 20 moles acetylene per mole of isobutyric acid. 30 Liters of acetylene were introduced in an hour. The stay time of the reactants in the catalyst zone was 3.5 sec. The temperature in the catalyst zone was measured with thermocouples at two points: at the entrance to the catalyst and at the middle of the bed. Samples for analysis were aspirated from the gas stream and analyzed for acidity, saponification and degree of unsaturation. The reaction product was collected in a series of receivers cooled to −20° to −78°. The product in the receiver was analyzed, purified by washing with dilute sodium carbonate solution and water, and finally dried and rectified. Catalyst was prepared by depositing zinc isobutyrate on active carbon. It contained 20% of zinc isobutyrate.
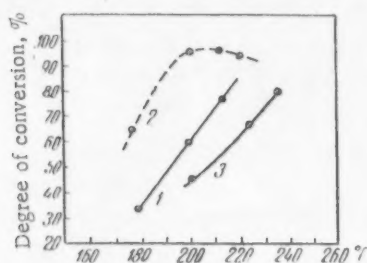
Fig. 1. Vapor-phase synthesis of vinyl isobutyrate:
1) percent conversion reckoned on isobutyric acid charged in; 2) on isobutyric acid consumed; 3) on butyric acid charged in.

Results of experiments carried out at various temperatures are plotted in Fig. 1 in which the amount of ester formed (as determined by analysis of condensate) is plotted on the ordinates. Curve 1 characterizes the rate of formation of ester at different temperatures; curve 2 corresponds to the true yield of vinyl isobutyrate after allowing for unreacted isobutyric acid entrained in condensate. Comparative data for n-butyric acid are represented on curve 3. It should be noted that curve 2 has a maximum(at ~200-210°)due, in the light of our considerations [10], to reduction in yield of vinyl isobutyrate owing to secondary reactions which are accelerated by further rise of temperature (increased rate of formation of the ethylidene ester followed by its decomposition, intensification of the role of direct breakdown of acid).

The experimental results indicate that vinyl isobutyrate can be prepared by the vapor-phase heterogeneous catalytic route with extremely high degree of conversion of the acid. The reaction goes rather more slowly than with acetic acid; for example, at 200° the conversion of acetic acid is close to 100%, but for isobutyric acid it is 62%. Butyric acid reacts more slowly than isobutyric acid (see diagram), probably due to increase in thickness of the adsorbed film consequent upon the lower vapor tension of an acid of normal structure. Vinyl isobutyrate was purified by washing, drying with calcium chloride, and fractionating in a short column.

We prepared vinyl isobutyrate by acidolysis of vinyl acetate at low temperature, as previously practiced in a number of cases by Adelman [12].

Starting substances for the synthesis were 1.2 moles of isobutyric acid, 6 times the quantity of vinyl acetate, 2% of mercuric acetate (on weight of isobutyric acid) and 0.5% of sulfuric acid. The reaction mixture remained at 30° for 24 hrs, after which sodium acetate was added to neutralize the inorganic acid. After filtration, the reaction mixture was fractionally distilled in a packed column with a working length of 25 cm, fitted with an attachment for incomplete condensation (a water-cooled microcondenser). The reflux number was ~ 5. 36.3 g

of a fraction boiling at 104° (~ 27% of the theoretical) was collected. The ester content, determined by bromination, was 99.8%.

The result of the foregoing experiment indicates that vinyl isobutyrate can be prepared without difficulties by acidolysis, as well as by vapor-phase reaction, although the acidolysis of vinyl acetate is associated with a lower effective conversion of the isobutyric acid brought into the reaction.

Physical properties of vinyl isobutyrate: b. p. 56° (135 mm); 104° (760 mm); n_D^{20} 1.4056; d_4^{20} 0.8915; found MR 31.405; calculated MR 31.095. Vinyl isobutyrate polymerizes with facility in presence of peroxide initiators to form a colorless solid with a vitrification temperature, measured in the Marei apparatus [19], of ~ 15°.

Vinyl isovalerate. This was prepared by us for the first time by the vapor-phase method using conditions similar to those described above for isobutyric acid. In proportion to the lower vapor pressure of isovaleric acid, the temperature in the vaporizer was raised to 84°. The temperature of entry of the vapor into the catalyst was 204-207°; that in the middle of the catalyst bed was ~ 240°. The acetylene/acid molar ratio and the duration of contact were the same as in the case of isobutyric acid. On the basis of analysis of the collected condensate, the yield of vinyl isovalerate was ~ 73% on the acid introduced and ~ 93% on the reacted acid.

After washing and drying, the crude vinyl isobutyrate was fractionated in a short column with a regular reflux. Vinyl isovalerate boils at 128.5° (760 mm); 50° (39 mm); n_D^{20} 1.414; d_4^{20} 0.8863; found MR 36.012; calculated MR 35.713.

Found %: C 65.56, 65.24; H 9.52, 9.54. $C_7H_{12}O_2$. Calculated %: C 65.58; H 9.36.

Vinyl isovalerate rapidly polymerizes when heated in presence of benzoyl peroxide. The polymer vitrifies at ~ 9°.

Vinyl caproate was prepared by two routs: 1) by acidolysis of vinyl acetate at 30 and 75-80°; 2) by vapor-phase catalysis. The acidolysis conditions were similar to those described above. Results of these experiments are presented in Table 1.

TABLE 1

| Expt. no. | Amount of reactants | | | | Reaction temperature in °C | Yield in % of theoretical |
| | vinyl acetate in moles | caproic acid in moles | mercuric acetate | sulfuric acid | | |
			in % of weight of caproic acid			
1	2.4	0.4	3.4	0.32	78—80	35
2	2.4	0.4	3.44	0.5	78—80	39
3	4.6	0.775	2.0	0.5	30	67

TABLE 2

| Expt. no. | Temperature in °C | | | acetylene acid ratio. (molar) | Duration of experiment in hrs | Yield (% of theory) | |
| | in vaporizer | in contact zone | | | | on acid introduced | on acid consumed |
		at inlet to catalyst	in middle of catalyst bed				
1	117	199—201	250	23 : 1	8.5	74.0	
2	112	211—214	250—260	30.6 : 1	10.3	68.4	83.8
3	114	191—193	240—241	25 : 1	11.5	85	90.4

In Table 1 the yield of ester is based on the analysis of the condensate after fractionation of the crude product. The product isolated by refraction was analyzed (bromination) at 83% vinyl caproate. Purification was evidently made difficult by the presence of a considerable amount of ethylidene esters, especially ethylidene acetate, formed by reaction with vinyl acetate of the acetic acid released during the process.

We effected the synthesis of vinyl caproate by vapor-phase heterogeneous catalysis under conditions similar to those described above. The catalyst contained 15.7% of zinc caproate on active carbon. As in previous vapor-phase syntheses, the duration of contact was 3.5 sec. The catalyzate entered a set of receivers cooled with a mixture of snow and salt and (the later ones) solid carbon dioxide. Results are presented in Table 2.
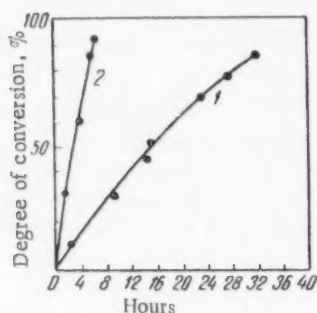
Fig. 2. Reaction of vinyl acetate with acetic acid:
1) catalyst, mercuric phosphate (2%); 2) catalyst,
mercuric sulfate (0.5%).

Yields were calculated on the basis of analysis of condensate. The products collected in the cooled receivers (−15 and −70°) were worked up separately.

The condensate from the first receivers contained (by analysis) 84.8% of vinyl caproate and 11.8% of acid (calculated as caproic). The product was washed with 0.5 N caustic alkali solution and fractionated in vacuo in a packed column provided with an attachment for incomplete condensation. A fraction analyzing at ∼ 100% vinyl caproate [b. p. 51-52° (9 mm)] was isolated in a yield of about 97% of the product subjected to purification.

The condensate from the second receiver contained a considerable quantity (∼ 20%) of acetaldehyde and ∼ 70% of vinyl caproate. In our opinion the presence of acetaldehyde is evidence of a secondary reaction — formation of ethylidene ester which cannot be stable in the vapor-phase catalytic zone. Isolation of pure ester from these condensates was likewise free of difficulties.

Vinyl caproate obtained from the main fraction by subsequent rectification had the following constants: b. p. 37° (3 mm); n_D^{20} 1.4220; d_4^{20} 0.8870; found MR 40.68; calculated MR 40.33. Vinyl caproate polymer is soft, rubbery and tacky; it vitrifies at ∼ −15°.

Various ethylidene esters can be formed on acidolysis of vinyl acetate. For the purpose of establishing the possible rate of formation of ethylidene esters under acidolysis conditions, we ran experiments in which vinyl acetate was directly treated with acetic acid in presence of mercury catalyst (sulfuric acid and mercuric phosphate). The reaction rate was established from the quantity of vinyl acetate consumed. Reaction temperature 75-80°. Results of these experiments (plotted in Fig. 2) show that addition of acid can proceed with considerable velocity.

TABLE 3

Expt. no.	Starting acid	Method of synthesis and yield of vinyl ester in %			
		acidolysis of vinyl acetate		reaction with acetylene	
		at 30°	at 75–80°	liquid-phase (w/o pressure)	heterogeneous catalytic
1	Isobutyric	27.0	---	3	86
2	Isovaleric	—	—	—	73
3	Caproic	67.0	35—39	---	70—84
4	Benzoic	44—50	—	---	90

We see from Fig. 2 that the addition of acid at the double bond can lead to appreciable fall in the yield of vinyl ester from acidolysis.

We also performed the acidolysis of vinyl acetate with benzoic acid and some other aromatic acids at 75-80°.

Conditions in these experiments were similar to those for caproic acid. The yield of vinyl benzoate was 44-50%.

Results of experiments on synthesis of vinyl isobutyrate, isovalerate and caproate are compared in Table 3. Corresponding data are also shown for vinyl benzoate, the conditions of vapor-phase synthesis of which have been described by us in the preceding paper [10].

The yields in Table 3 are calculated on the acid introduced into the reaction or passed through during heterogeneous catalysis. On the basis of acid consumed, the yields in vapor-phase synthesis reached 95%, 93%, and 90% of the theoretical for isobutyric, isovaleric and caproic acid, respectively.

The experimental results indicate that the vapor-phase method gives a higher degree of useful conversion and the product can be purified more simply. The reaction temperature in vapor-phase catalysis must be higher in the case of acid with a lower vapor pressure. We can also conclude that heterogeneous catalytic synthesis from acetylene and acid is the most expedient method of synthesis of the vinyl ester of caproic acid and probably also of vinyl esters of its closest homologs with a larger number of carbon atoms. This method excludes contamination with ethylidene esters which greatly complicate the purification of the monomer, and leads to a vinyl ester of very high purity.

Acidolysis of vinyl acetate, notwithstanding the development of secondary reactions, is quite suitable for the laboratory preparation of various vinyl esters, and may be of value in particular for the synthesis of esters of high-boiling acids.

In the examples discussed, the main factors in the development of secondary reactions which influenced the final result were the thermal stability of the acid (for the vapor-phase method) and the formation of ethylidene esters which occurs to a considerable extent (Fig. 2) in acidolysis with mercury catalyst. In the light of the results of the foregoing experiments and of the previously published experimental material on the reaction with benzoic and certain other acids [10], we consider that the following may be put forward as a general scheme of the processes possible in the wide temperature range under consideration:
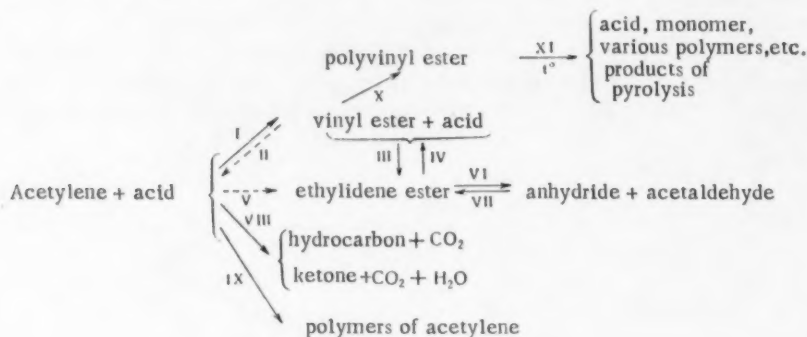
The scheme includes the main reactions; no account is taken in it of the existence of complexes with the catalyst whose intermediate formation is not in doubt at the present time.

The various directions of the reaction are realized in dependence, under the conditions employed, of primarily the activation energies and the corresponding temperature coefficient. The reactions are in part irreversible due to their consecutive occurrence. Rise of temperature accelerates the formation of vinyl ester but also intensifies the formation of ethylidene ester (III, V) and its breakdown (VI). Increased catalyst activity also increases the rate of I, III, and V, while slowing-down of the process markedly promotes reaction VIII. The thermal stability of the reactants at the reaction temperature (kinetics of thermal breakdown) is one of the most im-

portant factors governing the over-all effect of the reaction. Interaction of anhydride with acetaldehyde only occurs at low temperatures.

To a certain degree we can include the method of acidolysis of vinyl acetate in the above general scheme of main and secondary reactions, especially if we take into account the previously cited views of Adelman [12] on the mechanism of acidolysis reactions.

In the earlier methods of synthesis that we considered, the role of the catalyst was essentially similar: formation of the corresponding complex with acetylene and its subsequent breakdown under the reaction conditions under the influence of a third component introduced into the system (in the cases in question carboxylic acids or excess of acetylene). We assume that the use of salts of different metals as catalysts (mercury, zinc, cadmium, etc.) causes different types of activation of the acetylene molecule (at the π-bond or at the $C-H$ bond). This effect in turn determines the development of certain secondary reactions such as acetylene polymerization in the second of these cases.

Formation of metallic derivatives of acetylene by replacement of hydrogen is a manifestation of this type of reactivity. Further reaction of acetylides with acetylene under suitable conditions leads to formation of polymers of acetylene, notably cuprene:

$$\text{Acetylide + acetylene} \rightarrow \begin{array}{c} \text{vinylacetylene and} \\ \text{divinylacetylene} \end{array} \rightarrow \begin{array}{c} \text{cuprene and other polymers} \\ \text{of acetylene} \end{array}$$
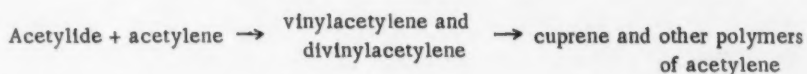
At the present time cuprene must be regarded as a representative of the class of three-dimensional porous, granular polymers (an ω-polymer). Various investigators have observed similar polymers in the polymerization and copolymerization of diolefinic derivatives, and sometimes also of monovinyl derivatives [20, 21].

SUMMARY

1. Vinyl isobutyrate, vinyl isovalerate and vinyl caproate were synthesized from acetylene and the corresponding acids by the heterogeneous catalytic, vapor-phase method. It was established that the useful conversion of acids in these reactions attains 90-95% of the theoretical when calculated on the acid consumed, and 70-90% when calculated on the acid introduced. Vinyl isovalerate has not previously been described.

2. Vinyl isobutyrate can be satisfactorily prepared not only by the vapor-phase method but also by the method of acidolysis of vinyl acetate.

3. It was established that the most suitable method of preparation of vinyl caproate, and probably also of esters of the nearest homologs of caproic acid with a larger number of carbon atoms, is the heterogeneous catalytic method, which avoids contamination with ethylidene esters. The latter considerably complicate the purification of vinyl caproate.

4. Experiments on reaction of vinyl acetate with acetic acid in presence of mercury catalyst showed that the addition reaction can take place with considerable velocity.

5. Secondary reactions are discussed with reference to the expediency of employing a given method to obtain maximum useful conversion of the acid and to the possibility of isolation of the ester in the pure form.

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BRIEF COMMUNICATIONS

POTENTIOMETRIC METHOD OF DETERMINATION OF SODIUM IONS WITH THE HELP OF THE GLASS ELECTRODE WITH SODIUM FUNCTION

B. E. Goremykin and P. A. Kryukov

The work of Nikolsky and his school [1-4] on the theory of the glass electrode, in particular the investigation by Schults [2] of glass electrodes with sodium function (GES), suggested their application for analytical purposes. This possibility was confirmed in later investigations of the stability and reproducibility of GES potentials [5] and in preliminary results of their application to the determination of $Na^{\cdot}$ concentration in natural waters [6].

An important condition for the exact determination of $Na^{\cdot}$ with the help of the GES is the establishment of the possibility of measurement both of the activities and of the activity coefficients of $Na^{\cdot}$ ions, although it is well known that only the mean corresponding magnitudes of the electrolytes possess strict thermodynamic value. For the purpose of measurement of a_{Na}, it was arbitrarily assumed, on the basis of work by Harned [7] and Taylor [8], that $\gamma_{Na^{\cdot}} = \gamma_{Cl^{\cdot}} = \gamma_{\pm} NaCl$ in dilute solutions of NaCl. The validity of this assumption is confirmed to some extent by emf measurements (E) of cells:

$$\text{Glass electrode} \quad | \text{ Solution of NaCl (m) } || \text{ KCl} | \text{Hg}_2\text{Cl}_2 | \text{Hg} \qquad \text{(I)}$$
$$\text{sat.}$$
$$\text{Ag} | \text{AgCl} \quad | \text{ Solution of NaCl (m)} || \text{ KCl } | \text{Hg}_2\text{Cl}_2 | \text{Hg} \qquad \text{(II)}$$
$$\text{sat.}$$
$$\text{Glass electrode} \quad | \text{ Solution of NaCl (m)} | \text{AgCl} | \text{ Ag} \qquad \text{(III)}$$
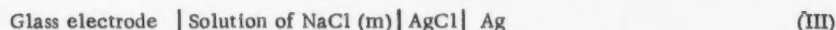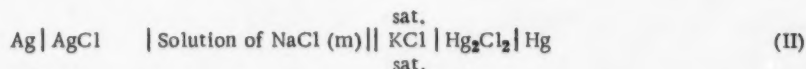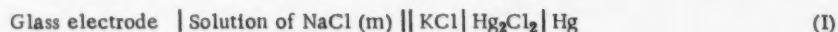
at various molalities (m) of standard solutions of NaCl (Table 1). In the graphical representation of results of measurements of E of cells I and II as functions of $\log a_{Na^{\cdot}}$ and $\log a_{Cl^{\cdot}}$, respectively, the straight-line plots in a given range of concentrations have equal angles of slope.

TABLE 1

Measurement of E of Cells in Standard Solutions

m_{NaCl} in element	E of elements			ΔE of elements		
	I	II	III	I	II	III
0.1	+0.0433	—0.0467	—0.0024	0.0161	0.0161	0.0322
0.05	+0.0272	—0.0628	—0.0356	0.0383	0.0382	0.0765
0.01	—0.0111	—0.1010	—0.1121	0.0169	0.0170	0.0339
0.005	—0.0280	—0.1180	—0.1460			

The possibility of measuring the activities of ions with the help of cells with a liquid junction was examined by investigation of mixtures of solutions of NaCl and $CaCl_2$ with constant ionic strength of $\mu = 0.1$. Activities were calculated on the basis of measurements of E in the solutions in question, using equations derived from calibration measurements in standard NaCl solutions.

TABLE 2

Activity Coefficients in Mixtures of Solutions of NaCl and $CaCl_2$

Expt. no.	Composition of mixture		$\gamma Na^{\cdot}$	$\gamma Cl'$	$\gamma \pm NaCl$
	m_{NaCl}	m_{CaCl_2}			
1	0.08998	0.003337	0.780	0.780	0.780
2	0.07499	0.008335	0.779	0.780	0.779
3	0.04998	0.01667	0.780	0.778	0.778
4	0.02500	0.02500	0.779	0.778	0.778

TABLE 3

Magnitudes of $\gamma_{Na^{\cdot}}$ in Na_2SO_4 Solutions

Expt. no.	$m_{Na_2SO_4}$	μ of Na_2SO_4 solution	$\gamma Na^{\cdot}$ found in Na_2SO_4 solution	$\gamma Na^{\cdot}$ assumed in NaCl solution	% deviation from assumed value
1	0.03333	0.1	0.736	0.778	−5.4
2	0.01666	0.05	0.813	0.823	−1.1
3	0.006666	0.02	0.877	0.875	+0.2
4	0.003333	0.01	0.904	0.904	±0.0
5	0.001666	0.005	0.929	0.929	±0.0
6	0.000666	0.002	0.951	0.953	−0.2
7	0.000333	0.001	0.966	0.966	±0.0

The data of Table 2 show that cells with liquid junction can be used for measurement of the empirical activities of ions; they also show that the magnitudes of $\gamma_{Na^{\cdot}}$ and $\gamma_{Cl'}$ remain identical in the given solutions with constant ionic strength, and agree with the value of $\gamma_{\pm} NaCl$.

Natural waters usually contain both Cl' ions and SO_4'' ions; we therefore tried to compare $\gamma_{Na^{\cdot}}$ in Na_2SO_4 solutions with the magnitudes of $\gamma_{Na^{\cdot}}$ in NaCl solutions over a wide range of ionic strengths.

It follows from Table 3 that an ionic strength slightly smaller than $\mu = 0.05$ can be considered the limit for solutions of NaCl and Na_2SO_4 up to which the magnitudes of $\gamma_{Na^{\cdot}}$ do not depend upon the composition of the

TABLE 4

Results of Determination of $Na^{\cdot}$ Concentration in Natural Waters with the Help of the Glass Electrode

Sample no.	Ionic strength of the water	$\dfrac{Ca^{\cdot\cdot} + "Ma"}{Na^{\cdot}}$	$\dfrac{SO_4''}{Cl' + HCO_3'}$	$Na^{\cdot}$ concentration in mg-equiv/liter		% difference
				by glass electrode	by zinc uranyl acetate method	
1	0.2473	0.5	0.3	130.50	129.80	+0.5
2	0.0362	2.0	0.9	8.91	8.73	+2.1
3	0.5330	6.0	0.9	163.70	165.20	−0.9
4	0.0478	<0.1	0.1	42.56	42.37	+0.5
5	0.0505	0.3	0.5	32.12	31.48	+2.0
6	0.0209	2.4	0.0	3.67	3.60	+2.0
7	0.0891	2.2	6.0	9.16	9.26	−1.1
8	0.0884	1.7	5.0	14.31	14.39	−0.6
9	0.1415	0.9	7.0	27.51	27.22	+1.2
10	0.1998	1.6	36.0	25.46	24.97	+2.0

solutions but only on the ionic strength. In mixtures of solutions of NaCl and Na_2SO_4 the divergence between the magnitudes of γ_{Na^+} in the mixture and in NaCl solution at $\mu = 0.05$ will still be smaller than in pure solutions. For natural chloride–sulfate waters, the nondependence of the values of γ_{Na^+} on composition can therefore extend in practice to an ionic strength of $\mu = 0.05$. We calculated the value of γ_{Na^+} for values of $\mu \leq 0.05$ with the equation

$$\log \gamma_{Na^+} = -\frac{0.506\sqrt{\mu}}{1 + 1.316\sqrt{\mu}} + 0.0521\mu, \tag{1}$$

used by Harned [9] for calculation of $\gamma_{\pm\,NaCl}$. In calculating the ionic strengths of natural waters it suffices to utilize the results of a shortened analysis of the water. The concentration of Na^+ ions, using the potentiometric method for their determination, was calculated from the equation

$$c_{Na^+} = \frac{a_{Na^+}}{\gamma_{Na^+}}.$$

Results of determination of Na^+ by the potentiometric method were compared with the results by the zinc uranyl acetate method [10] which is accepted as the standard method (Table 4).

Some samples were diluted with distilled water (sample 1, 10 times; sample 3, 20 times; samples 7 and 8, twice; sample 9, 3 times; and sample 10, 4 times). The mean deviation from the standard method was about $\pm$ 2%.

We applied this method to waters with pH > 6; more acidic waters were neutralized with gaseous ammonia in presence of neutral red as indicator. In the waters investigated, the ratio of equivalents $\frac{Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}{Na^{\cdot}}$ must not exceed 6.

SUMMARY

The possibility of determination of the concentration of ions in natural waters with the help of the glass electrode with sodium function was demonstrated.

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THE ORGANOMAGNESIUM COMPOUNDS OF SELENOPHENE

A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd

The organomagnesium compound of selenophene has not previously been described whereas the analogous compound of thiophene C_4H_3SMgX is well known and is fairly extensively used in a whole series of syntheses. In 1939 Umezawa [1] stated in his paper on the acylation of selenophene that an organomagnesium compound of selenophene cannot be prepared. Metallation of the selenophene nucleus with phenyllithium was effected by Yuryev and Sadovaya [2].

In connection with a study of tetraarylboron salts and an investigation of the possibility of effecting reaction of potassium fluoborate with RMgX in the heterocyclic series, we undertook an attempt at preparation of α-selenylmagnesium iodide. It was found that this organometallic compound is formed in ethereal solution from α-iodoselenophene and magnesium when operating in presence of ethylene bromide. α-Selenylmagnesium iodide reacts with CO_2 and benzophenone to give, respectively, α-selenophenecarboxylic acid and diphenyl-α-selenyl carbinol. It reacts as follows with potassium fluoborate:

$$\mathrm{KBF_4} + \overline{\underset{\mathrm{Se}}{\big\|\quad\big\|}} - \mathrm{MgI} \rightarrow \mathrm{KB}\left(-\overline{\underset{\mathrm{Se}}{\big\|\quad\big\|}}\right)_4$$
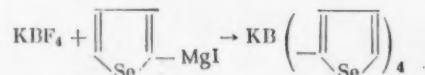
with formation of tetra-(α-selenyl)boron-potassium, whose properties resemble those of the thiophene analog [3]. Tetra(α-selenyl)boron-potassium precipitates rubidium ions from aqueous solutions, also (more completely) ions of cesium and quadrivalent ammonium.

EXPERIMENTAL

α-Selenophenecarboxylic acid. To 1 g of magnesium (100% excess) in a small quantity of absolute ether was added a few drops of ethylene bromide. After the reaction had commenced, an ethereal solution of α-iodo-selenophene was added dropwise in the course of 20 min. If the reaction started to quiet down, another few drops of ethylene bromide was added. The reaction mixture was then heated 30 min on a water bath, cooled, and poured onto solid carbon dioxide; it was then decomposed with 10% HCl; the aqueous layer was extracted with ether. The ethereal layer was treated with 10% sodium hydroxide solution. The alkaline solution was washed with ether and acidified with 25% HCl. α-Selenophenecarboxylic acid came down when the solution was cooled. The aqueous solution was extracted with ether, the ethereal extract was dried with sodium sulfate and the ether was distilled off. An additional small quantity of α-selenophenecarboxylic acid was obtained. Total yield 0.94 g (25% of theory). After recrystallization from water, the acid had m. p. 118-119°. A mixture with an authentic specimen of α-selenophenecarboxylic acid did not show a depression of melting point.

Diphenyl-α-selenyl carbinol. To the Grignard reagent prepared from 6.9 g of α-iodoselenophene and 1.3 g of magnesium (100% excess) was added, with ice cooling, an ethereal solution of 4.9 g of benzophenone. The reaction mixture was decomposed with dilute HCl; the ethereal layer was washed several times with water and dried over Na_2SO_4. The ether was then distilled off; the residual dark-brown oil crystallized when ligroine was added. The crystals were filtered and washed with ligroine; m. p. 119-120°. Yield 1.6 g (90% of the theoretical) of diphenyl-α-selenyl carbinol. After recrystallization from aqueous alcohol it melted at 122-123° (with decomposition).

Found %: C 64.98, 65.16; H 4.62, 4.46. $C_{17}H_{14}OSe$. Calculated %: C 65.18; H 4.50.

Tetra-(α-selenyl)boron-potassium. A Grignard reagent prepared from 25.5 g of α-iodoselenophene (prepared from freshly distilled selenophene and used immediately after distillation in vacuo) and 4.8 g of magnesium was poured off from the residue of magnesium into a suspension of 2.7 g of KBF_4 in absolute ether. The reaction mixture was shaken for 15-20 min. Heat was generated. Two layers formed. After heat had ceased to be released, the precipitate was filtered (No. 1 filter) and washed several times with absolute ether. The solid was freed of KBF_4 by dissolving in nitromethane. Absolute ether was added to the filtered solution to bring down tetra-(α-selenyl)boron-potassium; yield 1.4 g (11% reckoned on the KBF_4).

Found %: C 33.51, 33.38; H 2.36, 2.32. $C_{16}H_{12}Se_4BK$. Calculated %: C 33.70; H 2.12.

Tetra-(α-selenyl)boron-potassium forms colorless crystals, readily soluble in acetone and nitromethane; less readily soluble in water; insoluble in ether and benzene.

Tetra-(α-selenyl)boron-rubidium. Addition of RbCl solution to an aqueous solution of 0.2 g of tetra-(α-selenyl)boron-potassium in 45 ml of water brought down tetra-(α-selenyl)boron-rubidium. It was filtered, washed with water and dried in a desiccator over P_2O_5. Yield 0.17 g of the salt.

Found %: C 31.15, 31.01; H 1.98, 2.03. $C_{16}H_{12}Se_4BRb$. Calculated %: C 31.18; H 1.96.

Addition of CsCl solution or $(CH_3)_4NCl$ to the filtrate brought down the corresponding salts.

Tetra-(α-selenyl)boron-cesium. Addition to CsCl solution to an aqueous solution of tetra-(α-selenyl)boron-potassium led to precipitation of tetra-(α-selenyl)boron-cesium. The substance had the following analysis after filtration, washing with water and drying over P_2O_5:

Found %: C 29.18, 29.08; H 1.92, 2.04. $C_{16}H_{12}Se_4BCs$. Calculated %: C 28.95; H 1.82.

No precipitate is formed when $(CH_3)_4NCl$ solution is added to the filtrate; this indicates more complete precipitation of cesium ions by the tetra-(α-selenyl)boron ion than of rubidium ions.

SUMMARY

1. It was shown that the organomagnesium compound of selenophene can be prepared from α-iodoselenophene and magnesium when the reaction is performed in presence of ethylene bromide.

2. α-Selenylmagnesium iodide reacts with potassium fluoborate to form tetra-(α-selenyl)-boron-potassium.

The rubidium and cesium analogs are described.

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THALLATION OF DIBENZOFURAN*

V. P. Glushkova and K. A. Kocheshkov

As we showed for the first time [1], reaction of anisole or thiophene with trivalent thallium salts of organic acids leads to organothallium compounds of the type of $ArTlX_2$, contrary to the results of American workers [2] who treated dibenzofuran with thallium trichloride and obtained di-(4-dibenzofuryl)thallium (9% yield), i. e., a compound of the Ar_2TlX class. In the cases that we investigated [1] the yields reached 44-88% in a very much shorter reaction period (5-40 min instead of five or more hrs) and at very much lower temperatures.

It therefore appeared of considerable interest to compare the behavior of dibenzofuran toward trivalent thallium salts of organic acids and trivalent thallium halides. We showed that the reaction with dibenzofuran takes the course:

$$+ Tl(OOCR)_3 \rightarrow \quad\quad - Tl(OOCR)_2 + RCOOH \quad (1)$$
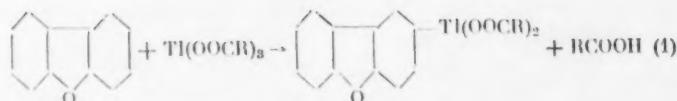
and leads to a 50% yield of 2-dibenzofurylthallium diisobutyrate, i. e., as we usually find, to the $ArTlX_2$ class. Formation of Ar_2TlCl (Gilman) may possibly result from disproportionation under drastic reaction conditions. Another interesting feature is the occurrence of thallation in the 2-position, and not in the 4-position as reported by Gilman and Abbott [2] in their work with thallium trichloride. Proof of this is furnished by the formation of 2-iodobenzofuran iodide (m. p. 111°) [3] by the action of diisobutyrate and not of 4-iodobenzofuran [2] with m. p. 69-72°. Moreover, the iododibenzofuran that we obtained was transformed by the usual route (via the organomagnesium compound) into the corresponding carboxylic acid with m. p. 252-253° (the literature gives 24 -247°**as the melting point of 2-dibenzofurancarboxylic acid [4], and 209-210° as the melting point of 4-dibenzofuran carboxylic acid [5]).

Such an entry of thallium into the para-position relative to the oxygen tallies with our earlier observation [1] that thallation of anisole gives p-anisyl thallium diisobutyrate. Arsenation of dibenzofuran [6] goes in the para-position but lithiation [7] and mercuration [5], in the ortho-position relative to the oxygen.

We converted 2-dibenzofurylthallium diisobutyrate into the corresponding bis-monochloroacetate (analysis for thallium and chlorine).

EXPERIMENTAL

Thallation of dibenzofuran. 4.65 g of thallium triisobutyrate was heated with 3 g of dibenzofuran (excess) to 110°. The reaction mixture melted completely at first but later solidified. After heating for 2 hrs, the cooled

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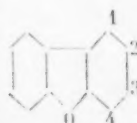
* (numbering as in Chemical Abstracts).

** Probably 246-247° — Publisher's note.

product was treated with a mixture of benzene and ligroine and suction-filtered to remove the excess of dibenzofuran. After additional washing on the filter with the same mixture, 3.9 g (50%) of a substance with m. p. 201-202° was obtained; after recrystallization from dichloroethane it had m. p. 206-207°.

Found %: Tl 38.44, 37.31. $C_{20}H_{21}TlO_5$. Calculated %: Tl 37.43.

Dibenzofurylthallium diisobutyrate is a white crystalline substance, stable in the air, highly soluble in pyridine, very much less soluble in chloroform, benzene and dichloroethane, poorly soluble in methanol, acetone, carbon tetrachloride and ethyl acetate in the cold, rather more soluble on heating, poorly soluble in ethyl alcohol (slight alcoholysis), insoluble in ether, ligroine and water.

Preparation of 2-iododibenzofuran from dibenzofurylthallium diisobutyrate. To 10.9 g (0.02 mole) of dibenzofurylthallium diisobutyrate in 150 ml of chloroform was added 5.08 g (0.02 mole) of iodine. The mixture was left until the next day by which time all of the material had gone into solution (the color persisted). The chloroform was removed, the residue was recrystallized once from methanol (with addition of carbon) and three times from ligroine. The melting point after the last two crystallizations was unchanged at 110.5-111°; 2-iododibenzofuran melts at 112° [3], and 4-iododibenzofuran melts at 69-72° [2].

Preparation of 2-carboxydibenzofuran from 2-iodobenzofuran. The 2-iodobenzofuran obtained in the preceding experiment was converted by the usual method into the corresponding organomagnesium compound in an ethereal medium by reaction with a small quantity of ethyl bromide and iodine. After carbonation with a mixture of solid carbon dioxide and ether and working up in the usual manner, the carboxylic acid (purified through the sodium salt) was recrystallized three times from alcohol (containing carbon). After the last two crystallizations, the melting point was unchanged at 252-253° (2-carboxydibenzofuran melts at 246-247° [4]; 4-carboxybenzofuran melts at 209-210° [5]).

Preparation of 2-dibenzofurylthallium bis-monochloroacetate from 2-dibenzofuryllithium diisobutyrate. To 0.93 g (0.002 mole) of dibenzofurylthallium diisobutyrate in 70 ml of methanol was added 1.1 g (0.002 mole) of monochloroacetic acid in 3 ml of methanol. The reaction mixture was filtered to clarify it, and the greater part of the solvent was removed by evaporation to leave 0.64 g of a white crystalline substance with m. p. 186-187° (with decomposition).

Found %: Tl 36.18, 36.24; Cl 12.71, 13.00. $C_{16}H_{11}TlO_5Cl_2$. Calculated %: Tl 36.49; Cl 12.74.

2-Dibenzofurylthallium bis-monochloroacetate is poorly soluble in the common organic solvents except methanol in which it is very soluble. Due to difficulties associated with crystallization, the analytical results refer to uncrystallized substance.

SUMMARY

1. It was shown, in contradiction to American authors (Gilman) that the thallation of dibenzofuran with thallium triisobutyrate leads to the $ArTlX_2$ class (and not to the Ar_2TlX class).

2. It was shown that thallation takes place in the para- and not in the ortho-position to the oxygen.

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*   In Russian.

SYNTHESIS OF β-CHLORO- AND β,β-DICHLOROVINYLALKYLDICHLOROSILANES

A. D. Petrov, V. F. Mironov, and D. Komanich

We earlier [1] developed a method of synthesis of β-chlorovinyltrichlorosilane (ClCH=CHSiCl$_3$) by dehydro-chlorination of β,β-dichloroethyltrichlorosilane in presence of a catalytic quantity of aluminum chloride. In the present investigation we established the optimum conditions of synthesis of ClCH=CHSiCl$_3$ and prepared its alkyl and alkoxy derivatives, including the difunctional (at the silicon atom) β-chlorovinylethyldichlorosilane.

Agre [2] obtained β,β-dichlorovinyltrichlorosilane (Cl$_2$C=CHSiCl$_3$) by pyrogenic condensation of trichloro-silane with trichloroethylene at 550°. In studying this method we observed that trichloroethylene can also be con-densed with alkyldichlorosilanes; this is an extremely simple route to the synthesis of dichlorodialkylsilanes with functional groups in the alkyl chain:

$$Cl_2C = CHCl + HSiRCl_2 \rightarrow Cl_2C = CHSiCl_2R + HCl,$$
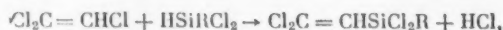
where R = CH$_3$ or C$_2$H$_5$.

The correctness of the above equation and the location of the chlorine atoms are confirmed by the agree-ment between the physical properties of the β,β-dichlorovinyltriethylsilanes prepared by Agre [2] and ourselves:

$$Cl_2C=CHCl \begin{bmatrix} \xrightarrow{HSiCl_3} Cl_3SiCH = CCl_2 \\ \xrightarrow[C_2H_5SiHCl_2]{} C_2H_5Cl_2SiCH = CCl_2 \end{bmatrix} \xrightarrow{C_2H_5MgBr} (C_2H_5)_3SiCH = CCl_2.$$
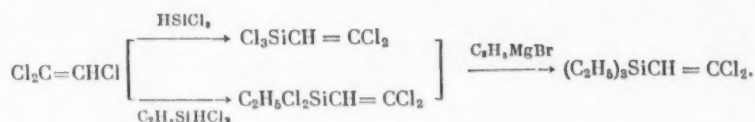
Both mono- and dichlorovinylalkyldichlorosilanes are probably of practical interest. Reference is made in one of the patents [3] to the high adhesive power of polysiloxanes containing chlorovinyl radicals and to their use in resin-bonded glass fiber cloths.

EXPERIMENTAL

β-Chlorovinyltrichlorosilane ClCH=CHSiCl$_3$. 511 g of β,β-dichloroethyltrichlorosilane [1] and 1 g of alu-minum chloride were placed in a one-liter flask fitted with a dephlegmator and a sloping condenser terminating in a receiver. A vacuum of about 140 mm was established in the system by means of a water jet pump. Heating of the flask led to vigorous evolution of gas (HCl) for about 30 min, after which liquid began to distil over rapidly at 120 mm. When $^2/_3$ of the contents of the flask had distilled over, an additional 0.5 g of aluminum chloride was added. Toward the end of the distillation, the vacuum and the heating were intensified in order to complete the removal of liquid. A black scum remained in the flask and solidified (4.5 g). 421 g of condensate was col-lected and rectified in a column; 3 g came over at 100 to 133°; the yield of β-chlorovinyltrichlorosilane was 340.5 g with b. p. 133-134° (79%, or 85% on the β,β-dichloroethyltrichlorosilane entering into reaction). In addi-tion, 30 g of an intermediate fraction (134-170°) was obtained. 37 g of the original Cl$_2$CHCH$_2$SiCl$_3$ was recovered; b. p.173-176°; the residue weighed 4.5 g.

A second experiment with 375 g of β,β-dichloroethyltrichlorosilane, but with a single addition of 1 g of AlCl$_3$ at the start of the reaction, led to a 64.6% yield of ClCH=CHSiCl$_3$, or 80% on the β,β-dichloroethyltri-chlorosilane entering into reaction.

TABLE

Serial no.	Formula of compound	Yield in %	B. p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.	Found in % C	Found in % H	Found in % Si	Found in % Cl	Calculated in % C	Calculated in % H	Calculated in % Si	Calculated in % Cl
1	$CH_3Cl_2SiCH=CCl_2$	27.8	163.8(752.1)	1.4893	1.4056	43.14	43.77	16.45: 16.20	1.69: 1.69	13.90: 13.71	67.58: 67.59	17.15	1.92	13.37	67.54
2	$C_2H_5Cl_2SiCH=CCl_2$	12	187.2 (740)	1.4930	1.3485	48.28	48.28	21.30: 21.35	2.70: 2.73	12.60: 12.45	—	21.44	2.69	12.53	63.31
3	$(CH_3)_3SiCH=CCl_2$	60	143.3 (744)	1.4605	1.0380	44.67	44.51	35.63: 35.74	6.06: 6.10	16.28: 16.46	41.71: 41.71	35.50	5.91	16.57	42.01
4	$(CH_3)_2C_2H_5SiCH=CCl_2$	40	32 (3)	1.4680	1.0331	49.28	49.02	39.30: 39.45	6.58: 6.60	15.25: 15.15	—	39.34	6.60	15.33	38.71
5	$CH_3(C_2H_5)_2SiCH=CCl_2$	60.5	60.5 (4)	1.4740	1.0348	53.55	53.53	41.07: 41.40	6.75: 6.91	15.79: 15.62	—	39.34	6.55	15.30	—
6	** $(C_2H_5)_3SiCH=CCl_2$	56	64 (3.5)	1.4786	1.0368	57.73	58.04	45.45: 45.67	7.76: 7.84	13.21: 13.09	33.25: 33.19	45.50	7.58	13.27	33.65
7	$(C_2H_5)(C_2H_5O)_2SiCH=CCl_2$	68.5	71.8 (3.5)	1.4512	1.0945	59.85	59.8	39.60: 39.65	6.50: 6.65	11.60: 11.75	—	39.50	6.63	11.54	29.15
8	$C_2H_5Cl_2SiCH=CHCl$	32	162.8 (752)	1.4739	1.2254	43.44	43.35	25.50: 25.22	3.84: 3.82	14.75: 14.90	25.50: 25.22	25.33	3.69	14.78	56.20
9	$(C_2H_5)(C_2H_5O)_2SiCH=CHCl$	46	71.5 (5)	1.4305	0.9936	54.64	54.87	46.06: 46.04	8.56: 8.57	13.40: 13.60	—	46.03	8.21	13.45	—
10	$(C_2H_5)_3SiCH=CHCl$	73	191.5 (751)	1.4637	0.9145	53.29	53.11	54.30: 54.25	9.80: 9.75	15.90: 16.00	—	54.35	9.69	15.89	20.05
11	$(C_2H_5O)_3SiCH=CHCl$	56	76.5 (5)	1.4200	1.0212	55.69	55.75	43.18: 43.28	7.75: 7.65	12.45: 12.49	14.04: 14.34	42.76	7.57	12.47	15.18

* Calculated on the basis of the magnitudes of the group refractions.

** Literature data: b. p. 97-99° (14 mm); n_D^{20} 1.4780 [2].

β,β-Dichlorovinylmethyldichlorosilane $Cl_2C=CHSi(CH_3)Cl_2$. A mixture of 412 g of trichloroethylene and 360 g of methyldichlorosilane was passed through a glass tube (diameter 25 mm, length 700 mm) heated in a tubular electric furnace to 560° ± 10°. The rate of flow was 1 drop per second. 583 g of condensate was obtained and was fractionated in a column to give 20 ml of CH_3HSiCl_2, 28 ml of $SiCl_4$, 70 ml of CH_3SiCl_3, 128 ml of $Cl_2C=CHCl$, and 130 ml (183 g) of $Cl_2C = CHSi(CH_3)Cl_2$; b. p. 164°; yield 27.8%. The heavy ends in the flask weighed 62 g. A similar reaction at 600° gave a yield of 16% of β,β-dichlorovinylmethyldichlorosilane.

β,β-Dichlorovinylethyldichlorosilane $Cl_2C=CHSi(C_2H_5)Cl_2$. Passage of a mixture of trichloroethylene (967 g) and ethyldichlorosilane (967 g) at about 520° ± 10° (other conditions being the same as previously) led to formation of β,β-dichlorovinylethyldichlorosilane in a yield of 12%; b. p. 186-188°.

β-Chlorovinyltriethoxysilane $ClCH=CHSi(OC_2H_5)_3$. 50 g of β-chlorovinyltrichlorosilane was added with stirring and cooling to a mixture of 36 g of absolute ethanol, 61 g of pyridine and about 200 ml of ether. The next day the white precipitate was filtered off and washed with ether. After removal of the filtrate, the liquid was distilled in vacuo to give 32 g of β-chlorovinyltriethoxysilane, b. p. 76.5-77° (5 mm); yield 56%. Compounds 7 and 9 (see table) were synthesized in similar fashion.

β-Chlorovinyltriethylsilane $ClCH=CHSi(C_2H_5)_3$. 49 g of β-chlorovinyltrichlorosilane was added with stirring and cooling to C_2H_5MgBr prepared in 250 ml of ether from 22 g of Mg and 120 g of BrC_2H_5,. The ether was later driven off from the flask, and the residue was heated on a boiling water bath for 8 hrs. After recovery of the ether, the contents were decomposed with water. The ether layer was dried with $CaCl_2$ and distilled to give 32 g of β-chlorovinyltriethylsilane; b. p. 191.5-192° (751 mm); yield 73%. Compounds 3 to 6 (see table) were synthesized under similar conditions. Compound no. 8 was of course not treated with water during the synthesis but was filtered off from the magnesium salts.

SUMMARY

A simple method of synthesis of β,β-dichlorovinylalkyldichlorosilanes was developed, and their alkyl and alkoxy derivatives were prepared.

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* Original Russian pagination. See C. B. translation.

SYNTHESIS OF TETRAKIS-[TRIALKYL(ARYL)SILOXY]TITANIUMS
IN PRESENCE OF TERTIARY AMINES

B. N. Dolgov and N. F. Orlov

A number of studies [1-5] have been devoted to the synthesis of polymeric organotitanium-silicon compounds, but little work has appeared on the monomeric compounds. The first organotitanium-silicon compound — tetrakis-(trimethylsiloxy)titanium — was prepared in a yield of 18% in 1955 [6] by reaction of trimethylsilanol with titanium tetrachloride in presence of ammonia. The same compound was later synthesized by reaction of sodium trimethylsilanolate with titanium tetrachloride. Recently we showed that tetrakis-[trialkyl(aryl)siloxy]titanium can be obtained by transesterification of alkyl orthotitanates with trialkyl(aryl)silanols in presence of catalytic quantities of metallic sodium [7].

In the present work we describe a new method of synthesis of tetrakis-[trialkyl(aryl)siloxy]titaniums $(R_3SiO)_4Ti$, based on reaction of trialkyl(aryl)silanes with titanium tetrachloride in presence of nitrogen bases (dimethylaniline, pyridine, etc.) as binders of hydrogen chloride.

$$4R_3SiOH + Ti \xrightarrow{\text{base}} (R_3SiO)_4Ti$$
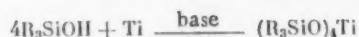
The yield of product is 40-95%.

Tetrakis-[trialkyl(aryl)siloxy]titaniums synthesized by this route are colorless liquids or crystals with a camphor odor, soluble in organic solvents.

EXPERIMENTAL

Synthesis of tetrakis-(methyldiethylsiloxy)titanium. To a solution (cooled to 0°) of 28.5 g (0.24 mole) of methyldiethylsilanol (b. p. 64° (30 mm); n_D^{20} 1.4204; d_4^{20} 0.8503) in 60 ml of benzene was slowly added (in presence of 18.3 g (0.235 mole) of pyridine) a solution of 11.4 g (0.06 mole) of titanium tetrachloride in 15 ml of benzene. After the whole of the titanium tetrachloride solution had been added, the reaction mixture was heated for an hour at 70-80°. The cooled reaction mixture was filtered and the filtrate (after removal of solvent) distilled in vacuo to give 12.0 g (38.8%) of tetrakis-(methyldiethylsiloxy)titanium $[CH_3(C_2H_5)_2SiO]_4Ti$ with b. p. 186° (6 mm); n_D^{20} 1.4565; d_4^{20} 0.9248.

Found %: Si 21.50, 21.22; Ti 9.43, 9.75. $C_{20}H_{52}Si_4O_4Ti$. Calculated %: Si 21.61; Ti 9.27.

Synthesis of tetrakis(triethylsiloxy)titanium. 1. In presence of pyridine. Starting with 53.0 g (0.4 mole) of triethylsilanol (b. p. 75° (24 mm); n_D^{20} 1.4340; d_4^{20} 0.8645), 30.6 g (0.39 mole) of pyridine in 10 ml of benzene, with addition of 19 g (0.1 mole) of titanium tetrachloride in 15 ml benzene under the same conditions, we obtained 26 g (45.5% of the theoretical) of tetrakis(triethylsiloxy)titanium $[(C_2H_5)_3SiO]_4Ti$; b. p. 227-230° (7 mm); m. p. 95-97°.

Found %: Si 19.33, 19.43; Ti 8.52, 8.20. $C_{24}H_{60}Si_4O_4Ti$. Calculated %: Si 19.61; Ti 8.36.

2. In presence of dimethylaniline. Tetrakis(triethylsiloxy)titanium was prepared in similar fashion from 26.4 g (0.2 mole) of triethylsilanol and 9.5 g (0.05 mole) of titanium tetrachloride in presence of 23.6 g (0.196 mole) of dimethylaniline. The yield of product was 23 g (89.5%); b. p. 195-198° (4 mm); m. p. 93-95°.

Synthesis of tetrakis(triphenylsiloxy)titanium. 16.9 g (0.06 mole) of triphenylsilanol and 2.84 g (0.015 mole) of titanium tetrachloride in 60 ml of benzene in presence of 4.6 g (0.06 mole) of pyridine gave tetrakis-(triphenylsiloxy)titanium which was isolated after decomposition of the pyridine hydrochloride with 5% KOH solution. 17 g (96.5%) of a finely crystalline solid was collected. After recrystallization from boiling o-xylene it had m. p. ~ 480°.

Found %: Si 9.50, 9.41; Ti 4.42, 4.23. $C_{72}H_{60}Si_4O_4Ti$. Calculated %: Si 9.76; Ti 4.16.

SUMMARY

1. Tetrakis-[trialkyl(aryl)siloxy]titaniums were synthesized by reaction of trialkyl(aryl)silanols with titanium tetrachloride in presence of nitrogenous bases.

2. Three tetrakis-[trialkyl(aryl)siloxy]titaniums were prepared and characterized.

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* Transliteration of Russian — Publisher's note.
** Original Russian pagination. See C. B. translation.

THE DISPROPORTIONATION OF TRIALKYLSILANES

S. N. Borisov, M. G. Voronkov, and B. N. Dolgov

Catalytic transformations of trialkylsilanes have hardly been studied. Boiling of $(C_3H_7O)_3SiH$ with 60 mole% of $AlCl_3$ is reported [1] to give $(C_3H_7O)_4Si$ in 20% yield. It has also been suggested [2] that $(CH_3)_3SiCl$ is reduced by aluminum borohydride according to the scheme:

$$6\,(CH_3)_3SiCl + 2Al(BH_4)_3 \rightarrow 6\,(CH_3)_3SiH + 3B_2H_6 + 2AlCl_3.$$
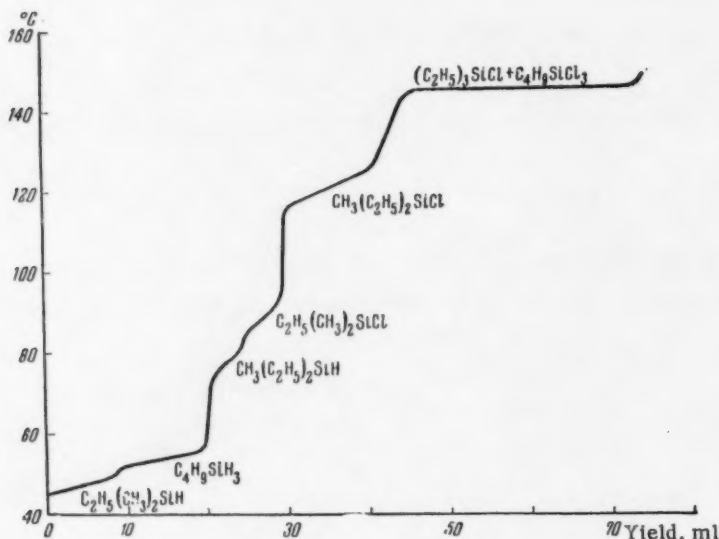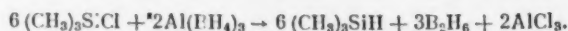
Fractional distillation curve of products of reaction of $n\text{-}C_4H_9SiCl_3$ with methyldi-ethylsilane in presence of 1.3 mole% of $AlCl_3$.

Nevertheless, the product, originally assumed to be trimethylsilane, was a three-component mixture due, in the authors' opinion, to a secondary reaction:

$$2(CH_3)_3SiH \xrightarrow{AlCl_3} (CH_3)_2SiH_2 + (CH_3)_4Si.$$
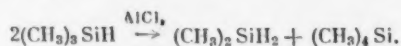
Reaction of $(CH_3)_3SiH$ with $AlCl_3$ was not, however, studied separately.

We recently described the reduction of alkylhalosilanes by triethylsilanes [3]:

$$R_nSiX_{4-n} + (4-n)(C_2H_5)_3SiH \xrightarrow{AlCl_3} R_nSiH_{4-n} + (4-n)(C_2H_5)_3SiX. \tag{1}$$
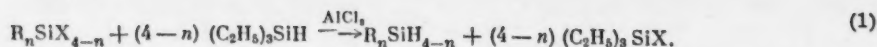
Starting from butyltrichlorosilane we obtained a nearly quantitative yield of n-$C_4H_9SiH_3$ and $(C_2H_5)_3SiCl$. It was expected that the replacement of triethylsilane by other trialkylsilanes would lead to similar reactions. A more complex process took place, however, on reacting n-$C_4H_9SiCl_3$ with $CH_3(C_2H_5)_2SiH$ in presence of 1.3 mole% of anhydrous $AlCl_3$ (see diagram); the products, apart from n-butylsilane and methylethyltrichlorosilane, were $C_2H_5(CH_3)_2SiH$ and $(C_2H_5)_3SiCl$ (in considerable quantities), as well as $C_2H_5(CH_3)_2SiCl$. This led us to the conclusion that the starting methyldiethylsilane only partially enters into the reduction reaction and to a greater extent disproportionates under the influence of $AlCl_3$:

$$2CH_3(C_2H_5)_2SiH \rightarrow C_2H_5(CH_3)_2SiH + (C_2H_5)_3SiH. \tag{2}$$

Such a transformation is presumably facilitated by the low boiling point of $C_2H_5(CH_3)SiH$ (46°), due to which it is removed from the reaction zone, whereas the triethylsilane (b. p. 108°) enters into a reaction of conjugated hydrogenation—halogenation and is converted into $(C_2H_5)_3SiCl$ (b. p. 147°). In the present case, therefore, rearrangement does not affect the Si—H bond. At the same time pure methyldiethylsilane unexpectedly reacted differently:

$$4CH_3(C_2H_5)_2SiH \xrightarrow{4 mole \% AlCl_3} 2C_2H_5(CH_3)_2SiH + \\ + (C_2H_5)_2SiH_2 + (C_2H_5)_4Si. \tag{3}$$
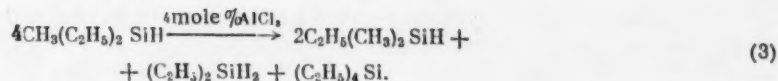
It was natural to assume that di- and tetraethylsilanes were formed by disproportionation of the triethylsilane originally formed according to Eq. (2) during prolonged action on it of $AlCl_3$, whose relative proportion in the reaction mixture steadily increased with progressive distillation of the $C_2H_5(CH_3)_2SiH$. Actually, on distillation over 10 mole% of $AlCl_3$, $(C_2H_5)_3SiH$ quantitatively undergoes disproportionation—symmetrization:

$$2(C_2H_5)_3SiH \xrightarrow{AlCl_3} (C_2H_5)_2SiH_2 + (C_2H_5)_4Si. \tag{4}$$
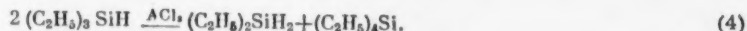
The Raman spectrum of the isolated diethylsilane contained frequencies of the C_2H_5 group at the Si atom (971, 1020, 1233 and 1462 cm^{-1}) and of the $> SiH_2$ group — 2130 cm^{-1} (ν Si—H) and 941 cm^{-1} (δ H—Si—H) [4].

Spectroscopic examination of the butylsilanes obtained according to Eq. (1) showed that they are substantially free of traces of diethylsilane. Consequently, triethylsilane evidently does not disproportionate under the conditions of hydrogenation.

EXPERIMENTAL

Methyldiethyl- and triethylsilanes were prepared by reaction of C_2H_5MgBr with CH_3SiHCl_2 and $C_2H_5SiHCl_2$, respectively (2:1 molar ratio of reactants). $CH_3(C_2H_5)_2SiH$ has b. p. 78.4°; n_D^{20} 1.3979; d_4^{20} 0.7054; yield 40%; $(C_2H_5)_3SiH$ has b. p. 108.3°; n_D^{20} 1.4123; d_4^{20} 0.7316; yield 60%.

Butyltrichlorosilane was prepared by reaction of n-C_4H_9MgBr with $SiCl_4$ in 1:2 molar ratio. n-$C_4H_9SiCl_3$ has b. p. 145.5°; n_D^{20} 1.4359; d_4^{20} 1.1610 yield 44.5%.

Aluminum chloride (anhydrous) was the purified separation from the Urnformer works.

Reaction of butyltrichlorosilane with methyldiethylsilane. A mixture of 28.2 g of n-$C_4H_9SiCl_3$, 45.2 g of $CH_3(C_2H_5)_2SiH$ (1:3 molar ratio) and 1 g (1.3 mole%) of $AlCl_3$ was boiled in the still of a rectifying column with an efficiency of 20 theoretical plates for 1.5 hr, the reflux temperature falling during this period from 75 to 44°. The following fractions were collected (see diagram): I — b. p. 45-49°, 6.4 g; ethyldimethylsilane [b. p. 45.7°; n_D^{20} 1.3783; d_4^{20} 0.6681; found H(Si—H) 0.99; 1.05%; calculated H 1.14%; II — b. p. 52-56°; 8.8 g; n-butylsilane [b. p. 54.1°; n_D^{20} 1.3912; d_4^{20} 0.6756; found H(Si—H) 3.23; calculated H 3.43%]; III — 74-94°; 8.4 g (n_D^{20} 1.4070; Cl 16.4% — mixture of methyldiethylsilane and ethyldimethylchlorosilane); IV — b. p. 116-126°; 6.4 g (n_D^{20} 1.4190; Cl 20.8% — impure methyldiethylchlorosilane); V — 126-143°; 7.3 g; VI — 143-147°; 27.6 g [n_D^{20} 1.4326; d_4^{20} 0.9624; Cl 32.9% — mixture containing 70.6% of $(C_2H_5)_3SiCl$ and 29.4% of $C_4H_9SiCl_3$].

<u>Reaction of methyldiethylsilane with $AlCl_3$.</u> A mixture of 30.6 g of $CH_3(C_2H_5)_2SiH$ and 1.5 g (3.8 mole%) of $AlCl_3$ was boiled in the still of a rectifying column for 3 hrs. The following fractions were collected: 9.8 g of ethyldimethylsilane (81.2%); 4.0 g of diethylsilane [b. p. 55.5°; n_D^{20} 1.3911; d_4^{20} 0.6820; found H(Si−H) 2.21%; calculated H 2.28%; 66.2%]; 2.7 g of unreacted methyldiethylsilane (conversion 91.2%) and 7.7 g of tetraethylsilane (b. p. 152.6°; n_D^{20} 1.4263; d_4^{20} 0.7729; 77.9%).

<u>Reaction of triethylsilane with $AlCl_3$.</u> 28.1 g of $(C_2H_5)_3SiH$ was slowly distilled in a column in presence of 3.2 g (10 mole%) of anhydrous $AlCl_3$ to give 6.2 g of diethylsilane (58.2%) and 17.1 g of tetraethylsilane (98%).

Raman spectrum of $(C_2H_5)_2SiH_2$* $\Delta\nu$ см$^{-1}$: 209 (1 d)* 245 (2 d), 295 (2d); 322 (1d), 581 (2 s), 606 (10)
668 (2 d) 702 (2 d); 766 (2d), 941 (5), 971 (6), 1020 (5), 1101 (1), 1233 (6), 1413(4), 1462(6),
2130 (15), 2740 (1), 2878 (10), 2897 (10), 2915 (3), 2941 (1), 2961 (10).

• d = diffuse; s = sharp

SUMMARY

It was shown that trialkylsilanes undergo disproportionation under the influence of $AlCl_3$. The nature of the rearrangement is governed both by the structure of the trialkylsilane and by the reaction conditions and the quantity of $AlCl_3$.

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• The spectrum was kindly measured by V. A. Kolesova.
• • Original Russian pagination. See C. B. translation.

DETERMINATION OF THE DEGREE OF UNSATURATION OF
ISOPENTANE–ISOPRENE–ISOAMYLENE MIXTURES BY BROMOMETRIC METHODS

B. A. Kazansky, O. D. Sterligov, A. P. Belenkaya, G. Ya. Kondratyeva,

and P. S. Pavlova

Catalytic dehydrogenation of isopentane gives a catalyzate consisting mainly of five components: the starting isopentane, three isoamylenes and isoprene. No specific method of analysis of such mixtures is known as yet. The commonest methods of determination of olefins are the bromometric methods of Rosenmund, Kaufman-Halpern and McIlliney -Virabyants [1, 2]. The latter method attempts to take into account the substitution reaction proceeding simultaneously with the addition of bromine. These secondary processes are governed not only by the bromination conditions but also by the structure of the olefin, due to which there are no standard condition for quantitative addition of bromine to a mixture of olefins. If the investigated mixtures contain conjugated dienic hydrocarbons, they rapidly add on one molecule of bromine, then slowly react with a second molecule, and the value found for the degree of unsaturation of the diene usually slightly exceeds 100% reckoned on one double bond.

TABLE 1

Analysis of Mixtures

Mixture no.	Composition of mixture in wt.%						Unsaturation in %(H)					
	iso-pentane	2-methyl-butene-2	2-methyl-butene-1	3-methyl-butene-1	iso-prene	total unsaturation	R	error, in abs.%	H	error in abs.%	V	error in abs.%
30	55.3	24.2	10.0	5.0	5.5	44.7	46.6	+1.9	43.1	−1.6	41.9	−2.8
31	45.7	25.3	19.8	4.6	4.6	54.3	56.2	+1.9	51.6	−2.7	51.3	−3.0
32	59.3	25.0	10.0	0.7	40.7	40.7	43.1	+2.4	39.8	−0.9	37.4	−3.3
33	56.4	26.0	9.7	4.8	3.1	43.6	44.9	+1.3	41.0	−2.6	37.5	−7.1
34	49.1	25.8	10.2	4.6	10.3	50.9	53.7	+2.8	48.2	−2.7	47.2	−3.7
35	39.5	25.6	10.1	4.6	20.2	60.5	65.8	+5.3	57.6	−2.9	60.3	−0.2
36	44.3	25.6	10.0	15.0	5.1	55.7	58.3	+2.5	53.8	−1.9	49.8	−5.9
42	33.5	28.2	11.0	5.2	22.1	66.5	69.8	+3.3	64.5	−2.0	62.6	−3.9
43	47.2	25.6	9.7	4.6	12.9	52.8	56.0	+3.3	51.1	−1.7	49.2	−3.6
44	43.6	25.4	9.8	4.4	16.8	56.4	58.8	+2.4	54.8	−1.6	53.6	−2.8

Note. R — Rosenmund method; H — Halpern method; V — Virabyants method.

The objective of the present work was to make a comparative evaluation of the accuracy of methods of bromometric determination of the degree of unsaturation and to establish the most suitable method of analysis of the products of catalytic dehydrogenation of isopentane.

A check of the bromometric method of Rosenmund, Halpern and Virabyants on artificial mixtures showed that the method of Virabyants is unsuitable for their analysis since the error in the determination is variable and amounts to 7-8 abs.% (Tables 1 and 2). In the analysis of mixtures containing ~ 15% of isoprene, the error in the determination of the total unsaturation averages +2% by Rosenmund's method and −2 abs.% by Halpern's method

TABLE 2

Unsaturation of Hydrocarbons

Name of hydrocarbon	Unsaturation of hydrocarbon in wt.%					
	R	error in wt.%	H	error in wt.%	V	error in wt.%
2-Methylbutene-2	99.8	−0.2	98.9	−1.1	95.0	−5.0
3-Methylbutene-1	99.8	−0.2	98.8	−1.2	96.6	−3.4
2-Methylbutene-1	112.4	+12.4	103.2	+3.2	92.2	−7.8
Isoprene	106.5	+6.5	104.6	+4.6	100.8	+0.3

TABLE 3

Determination of Isoprene and Calculation of Isoamylenes Content

Mixture no.	Composition of mixture in weight%			Total unsaturation	Isoprene found (v)	Error in abs.%	Calc. wt.% of isoamylenes					
	iso-pentane	iso-amylene	isoprene				unsaturation (calc. with application of factor α)		concentration of isoamylenes (H_3)			
							R	H	R	error in abs.%	H	error in abs.%
31	47.7	49.7	4.6	54.3	4.6	0.0	54.0	53.7	49.4	−0.3	49.1	−0.6
32	59.3	40.0	0.7	40.7	1.2	+0.5	41.4	41.4	40.2	+0.2	40.2	+0.2
33	56.4	40.5	3.1	43.6	3.7	+0.6	43.1	42.6	39.4	−1.1	38.9	−1.6
34	49.1	40.6	10.3	50.9	10.3	0.0	51.5	50.1	41.2	+0.6	39.8	−0.8
35	39.5	40.3	20.2	60.5	20.9	+0.7	63.2	59.9	42.3	+2.0	39.0	−1.3
36	44.3	50.6	5.1	55.7	5.6	+0.5	56.0	56.0	50.4	−0.2	50.4	−0.2
42	33.5	44.4	22.1	66.5	21.8	−0.3	67.0	67.0	45.2	+0.8	45.2	+0.8
43	47.2	39.9	12.9	52.8	12.0	−0.9	53.7	53.1	41.7	+0.8	41.1	+0.2
44	43.6	39.6	16.8	56.4	17.2	+0.4	56.4	56.9	39.2	−0.4	39.7	+0.1

TABLE 4

Determination of Unsaturation of Catalyzates (in wt%)

Catalyzate no.	Without application of factor α			With application of factor α		
	R	H	deviation in abs.%	R	H	deviation in abs.%
1	57.1	52.5	4.6	54.8	54.6	0.2
2	37.5	35.3	2.2	36.0	36.7	0.7
3	47.8	43.3	4.5	45.9	45.0	0.9
4	34.4	32.2	2.2	33.0	33.5	0.5
5	50.1	45.2	4.9	48.1	47.0	1.1
6	59.2	54.6	4.6	56.8	56.8	0.0
7	27.7	25.5	2.2	26.6	26.5	0.1

(Table 1); this is associated with the experimental conditions and the structure of the olefin (Table 2). It was found possible to allow for the analytical error in the methods of Rosenmund and Halpern by introducing a correction factor α, which was calculated as the mean ratio of the calculated content of unsaturated compounds (H_1) in the artificial mixture to the experimental value of its total unsaturation (H_2). For the Rosenmund method, α = = 0.96, and for the Halpern method, α = 1.04. Introduction of the factor α enables determination of the unsatura-

tion of artifical mixtures and isopentane dehydrogenation catalyzates with an accuracy of ±1% both by Rosenmund's and Halpern's method (Tables 3 and 4). The concentration of isoamylenes in the mixtures is calculated with the same accuracy by the formula (wt.%): $H_3 = \alpha H_2 - v$, where $\underline{v}$ is the content of isoprene.

Isoprene was determined by the colorimetric method of Robey and Wiese [3]; the error in the determination was 1 abs.% (Table 3).

SUMMARY

1. Depending on the composition of isopentane—isoprene—isoamylene mixtures, the accuracy of determination of the total unsaturation by the methods of Rosenmund and Halpern can vary by 1 to 3 abs.%. Introduction of correction factors enables the accuracy to be increased to ±1%. The method of Virabyants is unsuitable for analysis of these mixtures.

2. 2-Methylbutene-1 adds on more than one molecule of bromine under the investigated conditions of bromination.

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CATALYTIC HYDROGENATION OF METHYLCYCLOPROPYL KETONE

B. A. Kazansky, M. Yu. Lukina, and L. G. Salnikova

The three-membered carbon ring, when located in conjugation with certain unsaturated groupings, forms systems whose spectral characteristics are reminiscent of conjugated systems [1-3]. The analogy with such systems is supported by the catalytic hydrogenation of alkenylcyclopropanes which possess the type of structure in question [4, 5]. Here the conjugation effect is manifested in that, under conditions such that alkylcyclopropanes do not add on hydrogen with rupture of the C—C bonds of the three-membered ring, the "conjugated" alkenylcyclopropanes are hydrogenated and the ring is opened. It is characteristic that in this process the ring bonds affected are different from those attacked in the hydrogenolysis of alkylcyclopropanes, namely the bonds adjacent to the alkenyl substituent. The conjugation effect is not always manifested to the same degree; it depends on the reaction conditions and the type of catalyst. Thus, we know from the literature that conjugation does not play a part in the hydrogenation of alkenylcyclopropanes in presence of copper-chromium catalyst [6, 7] and plays a relatively minor part in presence of nickel catalysts [8]. We have found that palladium black [4] possesses special properties in this reaction and causes the conjugation effect to be developed with particular intensity, the exclusive reaction being the opening of the 3-membered ring with addition of hydrogen. Platinum black behaves like nickel [5] and gives both of the possible products of the reaction. Hydrogenation of vinyl cyclopropane, for example, may be represented by the following scheme:
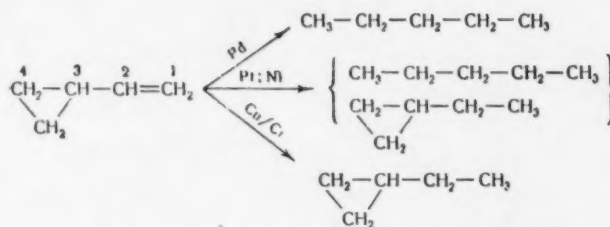
In the present work we studied, under mild conditions, the catalytic hydrogenation of methyl cyclopropyl ketone, a compound whose three-membered ring is conjugated with the carbonyl group. We know from the literature that in a number of cases the hydrogenation of this ketone* gives, apart from methyl cyclopropyl ketone, a carbinol with an open chain of carbon atoms [8, 9]. It is suggested that here also, just as in the case of hydrocarbons, the conjugation effect is responsible for the formation of the anomalous product. It is interesting that methylcyclopropyl ketone, as reported in [8], is susceptible to hydrogenation under conditions characteristic only of conjugated systems (by sodium in presence of ammonium sulfate in liquid ammonia). This reaction gives a mixture of pentanol-2 and pentanone-2. Only the carbonyl group was reduced when using copper-chromium catalyst [9], the three-membered ring remaining intact.

We have found that at room temperature in an alcohol medium in presence of platinum black, hydrogen addition to methylcyclopropyl ketone took place very slowly and ceased substantially after addition of about 1.3

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* Hydrogenation was performed at high temperature and pressure.

moles of hydrogen, even though some of the ketone remained unchanged. The products of hydrogenation were methylcyclopropyl carbinol and pentanol-2:

$$\underset{\substack{\diagdown CH_2 \diagup \\ CH_2}}{\overset{4}{CH_2}} - \underset{3}{CH} - \underset{\substack{| \\ CH_3}}{\overset{2}{C}} = \underset{1}{O} \xrightarrow[\text{H}_2]{\text{Pt}} \begin{cases} \underset{\substack{\diagdown CH_2 \diagup \\ }}{CH_2} - CH - \underset{\substack{| \\ CH_3}}{CH} - OH \\ \\ CH_3 - CH_2 - CH_2 - \underset{\substack{| \\ CH_3}}{CH} - OH \end{cases}$$
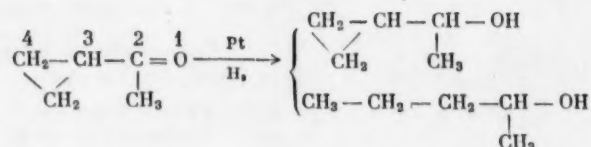
Formation of these carbinols may be accounted for by addition of hydrogen to the ketone at all of the possible positions in the conjugated system.

Hydrogenation with palladium black went differently. The reaction went at a considerably higher speed than with platinum black and stopped completely after absorption of one mole of hydrogen. The catalyzate boiled within a 0.1° range and, as was proven on the basis of its constants and the melting point of its 2,4-dinitrophenylhydrazone, it was pentanone-2:

$$\underset{\substack{\diagdown CH_2 \diagup}}{\overset{4}{CH_2}} - \underset{3}{CH} - \underset{\substack{| \\ CH_3}}{\overset{2}{C}} = \underset{1}{O} \xrightarrow[\text{H}_2]{\text{Pd}} CH_3 - CH_2 - CH_2 - \underset{\substack{| \\ CH_3}}{C} = O$$
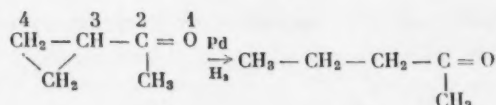
Consequently, in presence of palladium black, the three-membered ring of methyl cyclopropyl ketone is fully opened at room temperature, while hydrogenation occurs only at the ring (3,4-position) and does not affect the carbonyl group. This experiment again demonstrates the specificity of palladium as a hydrogenation catalyst for the three-membered ring conjugated with unsaturated groupings.

EXPERIMENTAL

Methylcyclopropyl ketone had the following constants: b. p. 111.5-112.0° (760 mm); n_D^{20} 1.4250; d_4^{20} 0.8995; m. p. of semicarbazone 121-122°. Literature data for the constants of the ketone and for compounds that can be formed by its hydrogenation are listed in Table 1. The experimental procedure and the catalysts have been described before [4, 5].

TABLE 1

Name of compound	B. p. in °C (760 mm)	n_D^{20}	d_4^{20}	M. p. in °C
Methylcyclo-propyl ketone [10]	112—112.5	1.4246	0.8987	of semicarbazone 120—122
Pentanone-2 [11]	101.7	1.3895	0.80639	of 2,4-dinitro-phenylhydrazone
Pentanol-2 [12]	119.8	n_D^{15} 1.40592	d_4^{15} 0.81319	
Methylcyclo-propyl carbinol [9]	122.5	1.43160	0.88860	

Hydrogenation in presence of platinum black. Components were 17.6 g (20 ml) of methylcyclopropyl ketone, 0.2 g of platinum black and 40 ml of alcohol. After addition of hydrogen in quantity equivalent to 1.3 moles, hydrogenation substantially ceased. The mean rate of hydrogenation was 21 ml/hr. After being washed and dried, the catalyzate was fractionally distilled in a column with an efficiency of 40 theoretical plates. Results are in Table 2.

TABLE 2

Fraction	B. p. in °C	Wt. in g	n_D^{20}	d_4^{20}
I	112.0—113.0	6.0	1.4228	0.8955
II	113.0—122.0	1.1	1.4173	0.8569
III	122.0—123.0	8.0	1.4300	0.8845
Residue		1.4	—	—
Losses		1.1	—	—

Comparison of the data of Tables 1 and 2 shows that fraction I is methylcyclopropyl ketone with a small admixture of pentanol-2; fraction III is methylcyclopropyl carbinol with a small admixture of pentanol-2; fraction II is an intermediate fraction.

Hydrogenation in presence of palladium black. 17.6 g (20 ml) of methylcyclopropyl ketone was taken with 0.2 g of catalyst and 40 ml of alcohol. The mean rate of hydrogenation was 64 ml/hr. Hydrogen was taken up in quantity equivalent to one mole. The catalyzate (after washing and drying) was distilled in a column with an efficiency of 40 theoretical plates. The catalyzate had b. p. 101.7-101.8° (760 mm); n_D^{20} 1.3896; d_4^{20} 0.8067; it gave a precipitate with sodium bisulfite and 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone had b. p. 141°. Comparison of the constants with the data of Table 1 shows that the catalyzate is pentanone-2.

SUMMARY

Considerable differences were found in the behavior of methylcyclopropyl ketone when hydrogenated in presence of platinum black and palladium black.

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* Original Russian pagination. See C. B. translation.

THE ACTIVE PRINCIPLES OF GINSENG

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E. S. Zyakhog, and V. F. Cherny

The chemical nature of the active principles of ginseng has not hitherto been elucidate in spite of the numerous studies in this field. Preparations previously isolated by various workers (panaxin, panatoxin, panaquilon and panaxozid*) were separated from ginseng extract by reaction with strong chemical reagents at high temperatures. It can be assumed that these preparations are mixtures mainly containing products of breakdown and oxidation.

In our opinion, the most promising method of isolation of the active and (like all plant compounds) easily oxidized substances of ginseng is the chromatographic method. This method is based on the differing adsorptivities of the compounds and permits all investigations to be made without modifying the structure of the original substances. Preliminary experiments by Cherny showed that a ginseng extract from which panocid had formerly been obtained could be separated into three parts with the help of column chromatography. We thus have the possibility of resolving a mixture of the substances of ginseng extract into less complex mixtures and even into individual groups of substances. Since the nature of the substances in ginseng is obscure, both the adsorbent and the solvent must be selected empirically.

For investigation we took an aqueous alcoholic extract of defatted, preserved ginseng root. Some of the properties of this extract were studied. Extracts of ginseng with 20% alcohol are the most active. The extract contained up to 12-20% of reducing substances, and their quantity increased on keeping, evidently due to hydrolysis of the glucosidic substances. In this connection the action of the ginseng extract on the nervous system and on cardiac action was similar to the effect of cardiac glucosides. Their hydrolysis leads to splitting-off of sugars from the aglucone whose structure is based on the cyclopentanophenanthrene skeleton. This structure characterizes many biologically active natural substances (cardiac glucosides, steroids, saponins, etc.). Saponins were detected in ginseng extract a long time ago. Some of the substances isolated from ginseng extract contain nitrogen, half of which is nonprotein.

The nitrogen compounds include the majority of the known stimulants of the nervous system [alkaloids, amines (phenamine)], and the most important property of ginseng is its stimulating and tonic action; it is therefore possible that the active principles of ginseng include nitrogen compounds. On the basis of the foregoing considerations, we may assume that ginseng extract contains sugars, nitrogen compounds, and substances of the steroid and glucoside types.

For confirmation of the presence of these compounds, we made use of the color reactions of paper chromatography. Ginseng extracts give spot reactions with ninhydrin, antimony trichloride, p-dimethylaminobenzaldehyde, benzidine and α-naphthol. These reactions confirmed the presence in ginseng extract of sugars, amino compounds and steroids. The possibility of separation of these compounds was established by means of partition paper chromatography (using paper cylinders). The best solvent was the upper layer of a mixture of n-butyl alcohol—acetic acid—water. Further resolution of the substances of ginseng extract was effected in an alumina column. Elution was performed with alcohol. The eluate was collected fractionally. Fractions with identical color reactions and refractive indices were combined.

Removal of the solvent left a series of preparations the majority of which were white powders. Aqueous solutions of the preparations were characterized by their biological activity. This evaluation was carried out by the pharmacological laboratory of the Far Eastern Branch of the Academy of Sciences, USSR on the basis of factors

* Transliteration of Russian — Publisher's note.

characteristic of ginseng extract. Preparations C-1, C-3, and Sh-1 possess an activity similar to that of ginseng extract but 90-100 times stronger. These preparations are readily soluble in water and have a blue-violet color in ultraviolet light. This color is similar to that of a thin section of fresh ginseng root in ultraviolet light.

In conclusion we extend out thanks to I. F. Belikov for cooperation in our investigations.

SUMMARY

1. Color reactions with ninhydrin, antimony trichloride, p-dimethylaminobenzaldehyde, benzidine and α-naphthol can serve for the chemical characterization of ginseng extract.

2. Chromatographic techniques enable active preparations to be separated from ginseng extract.

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* Russian translation.
** In Russian.

SYNTHESIS OF BUTYL ALCOHOL CONTAINING THE RADIOACTIVE CARBON ISOTOPE C^{14}

Yu. B. Kryukov, V. K. Butyugin, L. G. Liberov, N. D. Stepanova
and A. N. Bashkirov

A general route to the synthesis of alcohols containing radiocarbon from $BaC^{14}O_3$ has been proposed [1]. This consisted in the carbonation of alkylmagnesium halide with carbon dioxide to form an acid, esterification of the latter, and reduction of the ester to alcohol by the Adkins' reaction over copper-chromium catalyst under pressure. Ethyl, propyl, isobutyl and hexyl alcohols were synthesized by this method. Yields were relatively low 40-70% calculated on the original barium carbonate.

Other drawbacks of the above method are the many steps and the complicated arrangements for the individual steps (reduction of radioactive substances in an autoclave at 400 atmos and isolation of the products). This prompted us to develop a new route that would give a high yield of the desired product and would be more convenient and safer to operate. The investigation enabled us to synthesize butanol$-1C^{14}$ in 94% yield according to the following scheme:

$$1. \quad C_3H_7Br \xrightarrow{Mg} C_3H_7MgBr \xrightarrow{C^{14}O_2} C_3H_7C^{14}OOMgBr \xrightarrow{NaOH} C_3H_7C^{14}OONa$$

$$2. \quad C_3H_7C^{14}OONa \xrightarrow[C_4H_9COOH]{LiAlH_4} C_3H_7C^{14}H_2OH$$
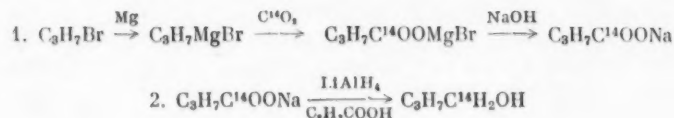
EXPERIMENTAL

First step: preparation of butyric acid. Taking into consideration the special features of work with radioactive carbon dioxide, we synthesized butyric acid in the vacuum apparatus shown in the diagram. Vessel 1 is intended for preparation of CO_2 by decomposition of carbonate with concentrated sulfuric acid; reaction flask 4
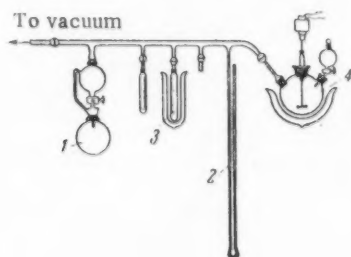
is intended for carbonation of the Grignard reagent. During preliminary work with inactive substances, we selected the optimum conditions for reaction with maximum utilization of $C^{14}O_2$. A previously prepared ethereal solution of propyl magnesium bromide (twofold excess), frozen with liquid nitrogen, was introduced into reaction vessel 4. In the lower vessel of the generator for preparation of $C^{14}O_2$ (vessel 1) was placed the necessary quantity of barium carbonate (about 9 g); concentrated sulfuric acid was poured into the upper flask. The apparatus was then degassed with an oil pump. The barium carbonate was decomposed by a

slow stream of sulfuric acid. The resultant carbon dioxide was frozen out in trap 3 (cooled with liquid nitrogen). During this operation the vacuum in the system was not upset and prevented solution of the CO_2 in the sulfuric acid. After the whole of the sulfuric acid had been added, the mixture was heated for an hour and shaken. The

yield of carbon dioxide was quantitative. The ethereal solution of propylmagnesium bromide was then frozen and the reaction flask was placed in a cooled bath at -50 to $-60°$. The stirrer was started, the cooling of trap 3 was suspended, and the gradually evaporating carbon dioxide entered the reaction flask. Absorption of CO_2 by the reaction mixture took place with great speed and did not lag behind the rate of evaporation from the trap. Absorption was substantially completed in 10 min. For the purpose of more complete utilization of the CO_2 remaining in the system, the CO_2 was frozen out in reaction vessel 4. The content of the flask was then melted, the tap was closed, and the mixture agitated for another 2 hrs. The completeness of utilization of the CO_2 was checked by readings of the manometer 2 at the start and finish of the experiment.

After nitrogen had been blown through the system, the organomagnesium complex was decomposed with 5% NaOH solution. The resultant precipitate was filtered off and washed on the filter with distilled water. The filtrate, containing radiocarbon-labeled sodium butyrate, was evaporated. The yield of sodium butyrate was 96% of the theoretical. It should be noted that the yield of butyric acid is 85-90% when the organomagnesium complex is decomposed with sulfuric acid and the butyric acid extracted with ether. The optimum yield of butyric acid reported in the literature is 77% [2].

Second step: preparation of butyl alcohol. The sodium butyrate (4.8 g) was dissolved in a mixture of 15 ml of inactive butyric acid and 105 ml of absolute alcohol and placed in a 1-liter three-necked flask fitted with a reflux condenser, stirrer and dropping funnel. An ethereal solution of lithium aluminum hydride (twofold excess) was added dropwise (with stirring) from a funnel, after which the mixture was stirred for another 3 hrs with heating on a water bath. The resultant alcoholate was decomposed with 20% sulfuric acid and the butyl alcohol was extracted with ether. The ether was driven off and the residue fractionated in a column to give 14.85 g of butyl alcohol or 93.5% of the theoretical calculated on the sodium butyrate and butyric acid. The yield of butyl alcohol, when calculated from the activity, was 94.3%.

This method can also be recommended for the synthesis of other alcohols of the aliphatic series. Further simplification of the technique is also possible. The organomagnesium complex $RC\overset{O}{\underset{\|}{-}}OMgX$, in the same way as an ester $RC\overset{O}{\underset{\|}{-}}OR_1$ and a salt, $RC\overset{O}{\underset{\|}{-}}ONa$, can be reduced to alcohol. This reduction is effected with lithium aluminum hydride directly after carbonation of the propylmagnesium bromide. In this case the yield of butyl alcohol is 50-60%.

SUMMARY

1. A new method is proposed for the synthesis of butyl alcohol labeled with radiocarbon C^{14} which is distinguished by simplicity and a yield of product.   Two stages are involved: organomagnesium synthesis of butyric acid and its isolation in the form of sodium butyrate, and reduction of the salt with lithium aluminum hydride. The method may be employed for synthesis of various alcohols containing radiocarbon C^{14}.

2. Labeled butyl alcohol can also be prepared without preliminary isolation of butyric acid by direct reduction of the organomagnesium complex $C_3H_7C\overset{O}{\underset{\|}{-}}OMgBr$ with lithium aluminum hydride.

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INVESTIGATIONS ON LACTONES AND LACTAMS

8. PREPARATION OF POLYVINYLPYRROLIDONE WITH PROTRACTED ACTION

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The interesting properties of polymers of vinylpyrrolidone are attracting the attention of investigators to an ever increasing extent. It is well known that polyvinylpyrrolidone with a molecular weight of about 40,000 is a good blood substitute [1]. The protein-like structure of this polymer has some similarity to that of the proteins of human blood.
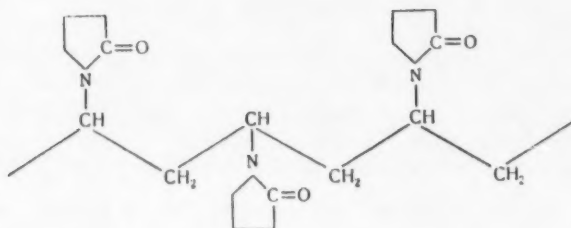
The literature also contains reports of the prolonging action of polyvinylpyrrolidone (PVP) (prolongation of the action of therapeutic agents on the human organism). The mechanism of the prolonging action of PVP has not been conclusively established; it is surmised that complexes are formed when this polymer is administered jointly with certain therapeutic agents, and these complexes are retained in the organism for a longer period than the agents alone [2]. Polymers of vinylpyrrolidone used as prolongers possess a higher molecular weight than PVP blood substitute. The literature does not contain a more precise physicochemical characterization of these preparations.

The objective of the present work was the study of polymers of vinylpyrrolidone with a relatively high molecular weight, the establishment of the characteristics of a preparation with prolonging action, and the establishment of the conditions for its preparation. For these purposes we studied the block polymerization of vinylpyrrolidone in presence of H_2O_2 and azodiisobutyronitrile, as well as in aqueous solution under the action of H_2O_2. The data obtained are presented in the table.

We see from the data in the table that in presence of azodiisobutyronitrile, polymerization goes at a lower temperature but very much more slowly than in presence of H_2O_2. The resultant polymers have a higher viscosity and are free of color or odor. Polymers obtained at above 100° nearly always possess an unpleasant smell and a yellowish color. Polymerization in presence of H_2O_2 in solution is preferable to block polymerization: 1) the process goes at relatively low temperature; 2) the yield of product is higher; 3) the polymer is colorless and free of odor. Physiological tests in the First Moscow Institute of Medicine [3] established that specimens with a relative viscosity of the 3% aqueous solution of 3.7 to 4.0 are good prolongers of action. The best specimen had a relative viscosity of 3.74, an osmotic pressure of 270 mm of water column, and an average molecular weight of ~ 50,000.

Polymerization of Vinylpyrrolidone Under the Influence of H_2O_2 and Azodiisobutyronitrile

| Serial no. | Initiator | Conditions for polymerization | | | | Polymer yield, % | Relative viscosity of 3% aqueous soln at 25° |
		solvent	amount of initiator, %	temperature, °C	duration in hrs		
1	Azodiisobutyro-nitrile	Absent	0.05	80	24	47	3.194
2	»	»	1.0	80	24	56	2.419
3	H_2O_2	»	0.76[a]	110[b]—170[c]	1.2	62	1.772
4	The same	»	1.00[a]	110[b]—150[c]	1.5	57	1.362
5	»	Water	0.23[a]	62 [d]	3	77	5.29
6	»	»	0.30[a]	61 [d]	3	65	3.74
7	»	»	0.31[a]	62 [d]	3	95	4.00[e]
8	»	»	0.33[a]	62 [d]	3	84	3.76

Note. a = quantity of initiator calculated on 100% peroxide; b = initial temperature; c = maximum temperature rise; d = maximum temperature of reaction mass; e = viscosity determined for 3.5% aqueous solution.

EXPERIMENTAL

1. Block polymerization. a) In presence of azodiisobutyronitrile. 5 g of vinylpyrrolidone and the requisite quantity of azodiisobutyronitrile were put into an ampoule which was then sealed and heated for 24 hrs at 80° ($\pm 1°$). The resultant polymer was dissolved in ethyl alcohol (5-6 ml), precipitated with diethyl ether (50 ml), then washed with ether (3-4 times) and dried in a vacuum-desiccator to constant weight. Unconsumed monomer (up to 30%) was recovered from the ether-benzene filtrates (see results in table).

b) In presence of H_2O_2. 40 g of vinylpyrrolidone and 1.3571 g of 30% H_2O_2 were heated rapidly to 110°. After 5-10 min the temperature had risen to 155°; it then fell quickly. The temperature was held for 1 hr at 110-115° by external heating. The resultant polymer was dissolved in benzene and precipitated with ethyl ether; it was then washed with ether (the polymer gradually changed from a viscous mass to a powder). Weight 31.65 g (yield 79.1%), relative viscosity of the 3% solution at 25° 1.36. 7.8 g of monomer was recovered from the benzene-ether extracts.

2. Polymerization in solution. To a solution of 40 g of vinylpyrrolidone in 80 ml of water was added a weighed amount of 30% H_2O_2 solution (0.37-0.38 g of 30% H_2O_2 for preparation of a prolonger) and 0.5 g of aqueous ammonia solution; the mixture was heated with stirring on a water bath for 3 hrs; the water was then removed in vacuo (residual pressure 20-30 mm); the polymer was dissolved in a little alcohol, precipitated with ethyl ether, washed three times with ether, and dried in a vacuum-desiccator (see table).

SUMMARY

1. Block polymerization of vinylpyrrolidone in presence of azodiisobutyronitrile and of H_2O_2, as well as polymerization in aqueous solution in presence of H_2O_2 were studied.

2. The physicochemical characteristics of a vinylpyrrolidone polymer effective as a prolonger were ascertained, and the conditions of preparation of such a polymer were established.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

18. HYDROCONDENSATION OF CARBON MONOXIDE WITH PENTENE-1 AND ISOMERIZATION OF THE LATTER TO PENTENE-2 UNDER THE CONDITIONS OF THIS REACTION

Ya. T. Eidus and M. B. Ordyan

In the present work we present the results of investigation of the behavior of pentene-1 under the conditions of hydrocondensation of carbon monoxide with olefins [1, 2]. Apparatus, catalyst and order of performance of the experiments remained the same as in preceding work [1, 2]. The catalyzates were fractionally distilled in a copper spiral-packed column with an efficiency of 40 theoretical plates. Pentene-1 was synthesized from C_4H_9Br and HCHO; the initially formed pentanol-1 [3] was converted to the acetate, and pyrolysis of the latter [4] gave a product with b. p. 29.9° (760 mm); d_4^{20} 0.6407; n_D^{20} 1.3712. Literature data [5]: b. p. 29.97° (760 mm); d_4^{20} 0.6405; n_D^{20} 1.3715. Experimental conditions and results are set forth in Table 1. All of the experiments were performed at 190° and atmospheric pressure.

TABLE 1

Experiment no.	Catalyst no.	Duration of expt., hrs	Amounts of reactants			Space velocity in			Amount of liquid catalyzate		% contraction of gas	Properties of condensate of gas			
			pentene-1 in ml	H_2 in liters (n.t.p.)	CO in liters (n.t.p.)	pentene-1	starting gas	of all of vapor-gas phase	in ml	in vol.% of original pentene-1		d_4^{20}	n_D^{20}	iodine no.	% content of unsaturated hydrocarbons
339	93	4	24	—	—	0.20	—	41	20	83.3	—	0.6408	1.3713	362	100
340	93 (regenerated)	8.5	50	6.3	—	0.20	24	65	45.5	91.0	88.9	0.6389	1.3695	165	45.6
341) 342}	94	22	129.5	13.3	2.2	0.20	24	65	113.3	87.4	68.0	0.6588	1.3830	176	59.4

In the experiments without gas (Table 1, expt. No. 339) the pentene-1 did not suffer any change at all over the catalyst. In experiments with pentene-1 in a hydrogen stream (Table 1, expt. No. 340) the vapor-gas phase had the composition: C_5H_{10} 63.1%; H_2 36.9%. 0.7 liter (n.t.p.) of end gas with the composition C_nH_{2n} 2.2%. H 97.0% and C_nH_{2n+2} 0.8% was collected. 5.6 Liters (n.t.p.) of hydrogen entered into reaction. Heating of the liquid catalyzate to 21° led to evolution of 370 ml of gas with the following composition (determined by chromatography on silica gel [6]): CH_4 1.9%; CH_{26} 17.5%; C_3H_6 30.4%; C_4H_{10} 24.8%; C_4H_8 25.4%.

The catalyzate (42 ml) was afterwards fractionated in a column. The yield and constants of the collected fractions are given in Table 2. We see that the main fraction III contained ~ 54% of pentene-2 and ~ 46% of pentane [5]; fraction I presumably consists mainly of pentene-1. Less than 10% of the catalyzate boiled below 35°. Fractions iI and III were qualitatively examined by the Raman spectrographic method.* The investigation

TABLE 2

Fraction no.	B. p. in °C (760 mm)	Yield in vol.%	n_D^{20}	d_4^{20}	Iodine no.	% content of unsaturated hydrocarbons
I	28 4—30.1	1.9	1.3685	—	—	—
II	30.1—35.8	17.1	1.3665	0.6356	192.4	53.8
III	35.8—36.0	64.6	1.3665	0.6356	192.2	53.7
Residue	55—176.5*	6.9	1 3945	0.6909	103.0	39.6
Losses	—	9.5	—	—	—	—

* Residue distilled from a Wurtz flask.

showed that fraction II consists mainly of n-pentane (401, 840 cm^{-1}), trans-pentene-2 (409, 484, 1674 cm^{-1}), and cis-pentene-2 (1660 cm^{-1}), and also contains pentene-1 (385, 435, 852, 1292, 1302, 1642 cm^{-1}). Fraction III consists of n-pentane (401, 840 cm^{-1}), trans-pentene-2 (409, 484, 1674 cm^{-1}) and cis-pentene-2 (859, 1660 cm^{-1}).

It follows from the foregoing data that in presence of hydrogen, pentene-1 isomerized to the extent of 40-45% to pentene-2, was hydrogenated to pentane to the extent of 35-40%, was converted to higher hydrocarbons to the extent of ~ 7%, and underwent hydrocracking to the extent of 2-2.5%. The latter is inferred from the quantity and composition of the gas evolved.

Pentene-1 in a stream of mixture of CO and H$_2$. In experiments with pentene-1 in a mixed stream of CO and H$_2$ (Table 1, Expts. 341 and 342), the vapor-gas phase had the composition: C$_5$H$_{10}$ 63.1%, H$_2$ 31.6%, CO 5.3%. 5.1 Liters of end gas with the following composition was collected: CO$_2$ 0.5%, C$_n$H$_{2n}$ 3.7%, CO 17.7%, H$_2$ 68.2%, C$_n$H$_{2n+2}$ 8.9%. Heating of the catalyzates of Expts. 341 and 342 to 21° yielded 1965 ml (n.t.p.) of gas with the following composition (chromatographic determination): C$_3$H$_6$ 7.2%, C$_4$H$_{10}$ 22.6%, C$_4$H$_8$ 70.2%. Amounts consumed [in liters (n.t.p.)] in the reaction were 10.0 H$_2$ and 1.3 CO. After the catalyzates (Expts. 341 and 342) had been freed of gas and dried, a fraction boiling below 40° and corresponding to pentenes and pentane was distilled off. Identical fractions obtained from both catalyzates were combined and their constants were determined. A total of 103 ml of catalyzate was taken for the fractionation. Results are detailed in Table 3 which shows that fraction I is mainly pentene-1 and fractions II and III are mixtures of nearly equal quantities of pentene-2 and pentane. 28.9 ml of residue boiling below 40° was obtained.
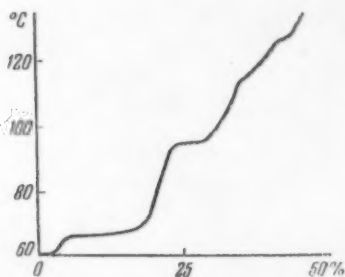
Curve of fractional distillation of the light portion of the hydrogenated residue with b. p. above 40° (Expts. 341 and 342).

It follows from the results obtained that in presence of H$_2$ and CO, pentene-1 undergoes hydrocondensation to the extent of 28-30%, isomerization to pentene-2 to the extent of 28-30%, and hydrogenation to pentane to the extent of ~ 25-27%, while it undergoes hydrocracking to the extent of ~ 3%.

* The Raman spectra were plotted and studied in the laboratory of the Spectroscopy Committee of the Academy of Sciences, USSR by V. T. Aleksan and Kh. E. Sterin to whom we express our thanks.

TABLE 3

Fraction no.	B.p. in °C (760 мм)	Yield in vol.%	n_D^{20}	d_4^{20}	Iodine no.	Content of unsaturated hydrocarbons in %
I	27.8—30.1	3.9	1.3698	0.6365	355.0	97.8
II	30.1—35.8	25.2	1.3680	0.6379	200.5	55.2
III	35.8—36.9	34.2	1.3680	0.6389	181.0	49.8
Residue	—	28.1	1.4100	0.7236	105.5	52.7
Losses	—	8.6	—	—	—	—

TABLE 4

Fraction no.	B. p. in °C (760 mm)	B. p. in °C (16 mm)	Yield in vol.%	n_D^{20}	d_4^{20}	C_n
I	60—70	—	16.5	1.3747	0.6574	C_6
II	70—90	—	4.0	1.3772	0.6650	$C_6 + C_7$
III	93—106	—	9.0	1.3875	0.6881	C_7
IV	106—124	—	8.0	1.3903	0.6925	$C_7 + C_8$
V	124—140	—	7.5	1.3977	0.7041	C_8
VI	140—170	—	10.5	1.4050	0.7171	(C_9)
VII	170—188	—	8.5	1.4130	0.7329	(C_{10})
VIII	—	94—136	12.5	1.4240	0.7543	—
IX	—	136—165	7.0	1.4340	0.7615	—
Residue	—	—	1.5	—	—	—
Losses	—	—	15	—	—	—

The residue (b. p. above 40°) in quantity of 28 ml was boiled over sodium (2 g) for 6 hrs, then hydrogenated (24 ml) in presence of Pt/C (2 cc) with addition of H_2PtCl_6; 1.4 liters of hydrogen was absorbed. 21.5 ml of hydrogenated product was obtained: d_4^{20} 0.7158; n_D^{20} 1.4052; this was fractionated (20 ml) in a column; the yield and constants of the fractions are given in Table 4. Fractionation of the light portion (up to 135°) of hydrogenated product is plotted in the diagram.

We see from Table 3 and the diagram that about 45 vol.% of the hydrogenated product boiled within the limits of 60-135° and consisted of paraffinic hydrocarbons (C_6 and higher), predominantly of normal structure with a small admixture of branched hydrocarbons (with one side CH_3 group), with even and odd numbers of C atoms in the molecule. Thus, on the diagram the lower plateau (b. p. 60°) corresponds to 2-methylpentane, while the middle area (b. p. 67-69°) corresponds to n-hexane. The ratio of these plateaus (1:4) is consistent with the constants of fraction I (Table 4). The top plateau (b. p. 95-97°) (fraction III, Table 4) corresponds to n-heptane, apparently admixed with some 2-methyl- and 3-methylhexanes. Raman spectrographic examination established that the main components of fractions I to III (Table 4) are n-hexane and n-heptane, respectively.

The results show that pentene-1 is considerably less active than butene-1 [7] in the hydrocondensation reaction, but more active than hexene-1 [8].

SUMMARY

1. In presence of H_2 and CO at 190°, pentene-1 undergoes hydropolymerization and hydrocondensation with CO to the extent of 28-30%, isomerization to pentene-2 to the extent of 28-30%, hydrogenation to pentane to the extent of 25-27%, and hydrocracking to the extent of 3%.

2. The hydrocondensate following hydrogenation is a mixture of saturated hydrocarbons of normal structure with a very small admixture of slightly branched paraffins.

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* Original Russian pagination. See C. B. translation.
** In Russian.

THE ACTION OF X-RAY RADIATION ON POLYAMIDES

B. L. Tsetlin and S. R. Rafikov

In recent years a large number of studies have been made of the problems of the action of ionizing radiations on polymers. Very little attention has been paid, however, to the transformations of polyamides (an impor-
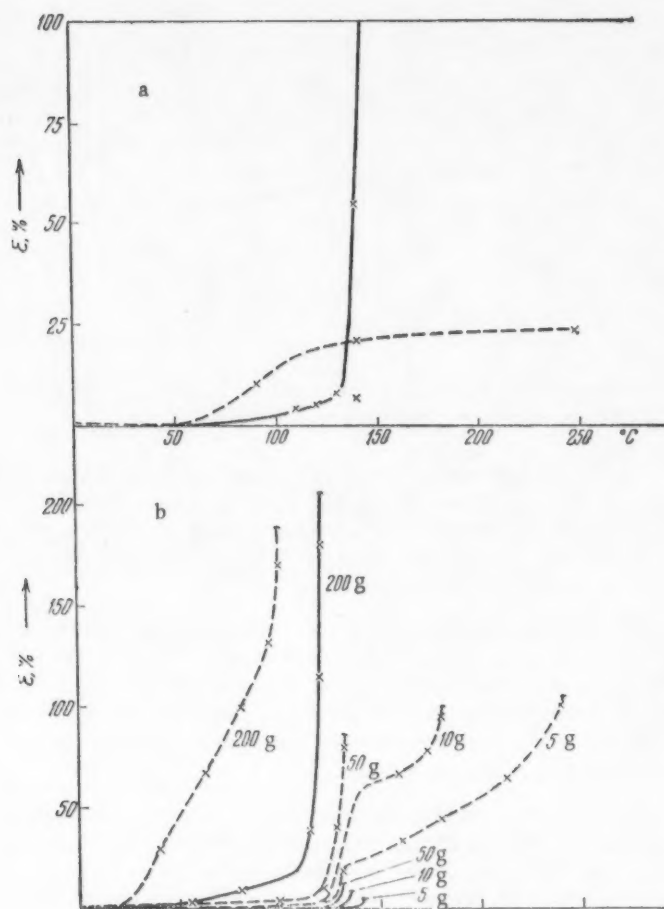
Fig. 1. Thermomechanical curves: a) compression; b) elongation of anid
G-669. ——) Nonirradiation specimen; -----) irradiated (20 hrs).
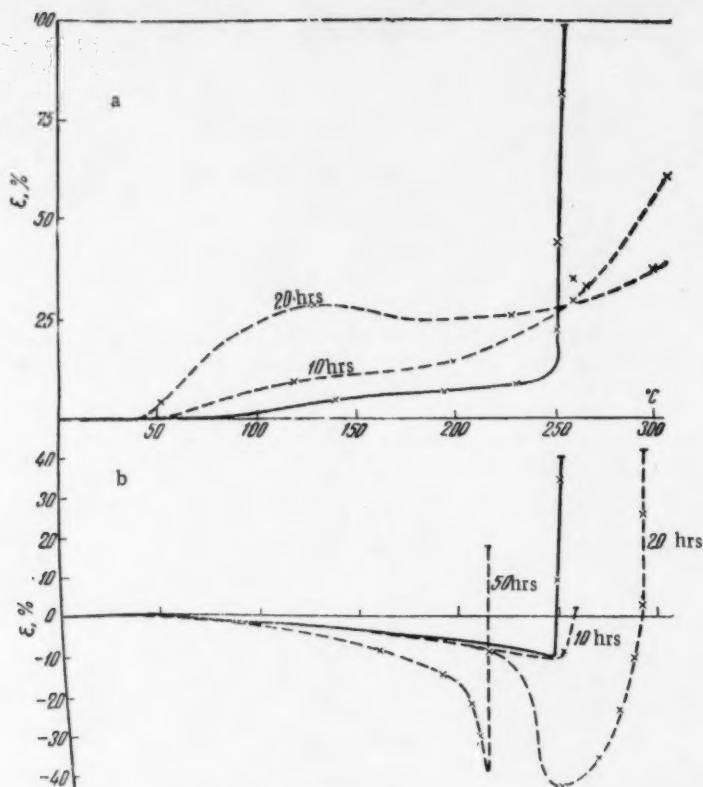
Fig. 2. Thermomechanical curves: a) compression; b) elongation of anid fiber. ———) Nonirradiated, — — —) irradiated specimens.

tant class of high-molecular polymers) under the action of radiations. Data in the literature about the transformations of polyamides are conflicting [1]. In the present work we investigate the action of high-intensity x-ray radiation on polyhexamethylene adipamide ("anid") and on the product of joint polycondensation of hexamethylenediamine with azelaic and adipic acids and caprolactam ("anid G-669") [2]. Specimens of anid G-669 were investigated in the unstretched form, those of anid in the stretched form.

The radiation source was a collapsible x-ray tube with a cylindrical tungsten cathode of the TrTs type designed by the Institute of Physical Chemistry of the Academy of Sciences, USSR [3]. The tube was operated with a maximum voltage of 80 kv and an anodic current of 200 ma. The strength of the dose was ~ $1.5 \cdot 10^{17}$ ev/cc · sec. The way in which the molecular structure of the polyamides changed was evaluated by the thermomechanical method with the help of an apparatus enabling thermomechanical curves to be plotted while the specimen was under continuous load throughout the whole of the test period [4].

Specimens of anid G-669 were irradiated in the form of circular discs with a diameter of 30 mm and a thickness of 1 mm. The duration of irradiation was 20 hrs. The specimens became yellow under the treatment and at the same time became more transparent; they ceased to be soluble either in alcohol or acetic acid. It was even impossible to dissolve them completely in formic acid containing a small proportion of HCl. The change in thermomechanical properties of anid G-669 under the action of the radiation is plotted in Fig. 1. Specimens with a diameter of 6 mm were irradiated for the purpose of plotting the compression curves. The load was 500 g and the diameter of the applied punch was 4 mm. Elongation curves were plotted on the basis of measurements on strips 0.15 mm thick; these were cut from films by a microtome (transverse cutting action). The elongating force applied in different tests ranged between 2 and 200 g (1.3-130 kg/cm^2).

Inspection of the thermochemical curves of compression of anid G-669 (Fig. 1a) reveals that the irradiated specimen does not melt at the melting point of the original polymer; it acquires limited deformation in the high-temperature region. This fact and the loss of solubility indicate that anid G-669 becomes cross-linked when irradiated. At the same time the irradiated specimen starts to be deformed at a temperature considerably lower than in the case of the original specimen. Similar regularities are revealed by the elongation curves (Fig. 1b). Under loads not exceeding 50 g (33 kg/cm^2) the nonirradiated specimens are substantially undeformed right up to the breaking point which occurs at the melting point. Under a load of 200 g (132 kg/cm^2) the specimens commence to stretch considerably earlier and break when the temperature is only about 100°. In this case the applied load is sufficient to cause recrystallization at a temperature considerably lower than the melting point (this phenomenon was considered in work by Kargin and Sogolova [5]). Irradiation leads to appreciable modification of the course of the thermomechanical curves. Even small elongating stresses (5 g) cause deformation of specimens at temperatures well below the melting point of the original polyamide. Under relatively high stresses (200 g) the specimens undergo considerable elongation even at temperatures of the order of 25-30°. Such a lowering of the temperature of initial deformation under compression and tension may be explained by destruction of the crystal structure of the polyamide such as occurs on irradiation of polyethylene and other crystalline polymers [6]. We also see from Fig. 1b, that under relatively high stresses the irradiated specimens rupture earlier than nonirradiated specimens. Under low stresses, however, the irradiated specimens, although they also start to deform earlier, than the non-irradiated ones, rupture at considerably higher temperatures which appreciably exceed the melting point. This shows that in the region of temperatures above the melting point, where crystallinity disappears completely, the mechanical properties of the polymer are governed by the cross-linkages developed by radiation-vulcanization.

Figure 2 illustrates the effect of irradiation on the thermomechanical properties of polyhexamethylene adipamide, the specimens of which were in the form of monofilaments with a diameter of 0.2 mm. Exposure periods were 10, 20 and 50 hrs. Compression curves were plotted under a load of 500 g, using a punch with a diameter of 4 mm. For these tests the fiber was cut into short threads which were inserted in the form of small pieces in the container of the apparatus. Elongation curves are based on measurements under load of 2 g on the monofilament specimen. Inspection of the compression curves (Fig. 2a) reveals a similarity between the nature of the change of thermomechanical properties of the anid and that of anid G-669. The irradiated specimens actually start to soften earlier than the nonirradiated. As with the first material, there is no appreciable change in deformation properties or irradiated specimens at the melting point of the original polymer. It is interesting that whereas in the low-temperature region (up to the melting point) the deformation of a specimen irradiated for 10 hrs is less than the deformation of a specimen irradiated for twice the period, in the high-temperature region the position is reversed, i. e., the curves intersect at the melting point of the original polyamide. The elongation curves (Fig. 2b) show that a nonirradiated specimen is substantially immune from deformation-relaxation right up to the melting point, at which point it ruptures immediately. In the case, however, of irradiated specimens, relaxation starts to be significant at a certain temperature which is well below the melting point, i. e., the linear dimensions of the specimens decrease. With increasing exposure period, this "critical relaxation temperature" falls. On the other hand, rupture of specimens irradiated for 10 and 20 hrs occurs at temperatures higher than the melting point. A specimen irradiated for 50 hrs breaks at a lower temperature; the strength of the fiber is evidently lowered by development of heterogeneity under prolonged irradiation. The observed changes of thermodynamic properties of irradiated anid fiber satisfactorily accord with the concepts of radiation-vulcanization of polyamides and the destruction of their crystallinity. Destruction of the crystallites makes possible the relaxation of the strains locked in the fiber due to its elongation (i. e., highly elastic strains); at the same time the development of cross-linkages governs the rise of temperature of rupture of the specimens which had received a certain mean dose of radiation. These "locked-in" stresses are not developed in a nonirradiated specimen.

SUMMARY

1. The effect of strong x-ray radiation on the thermomechanical properties of unstretched and stretched specimens of polyamides was investigated.

2. It was shown that processes of radiation-vulcanization and reduction of crystallinity take place in polyamides under the action of radiation.

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* Original Russian pagination. See C. B. translation.
** In Russian.

LETTERS TO THE EDITOR

THE RELATION BETWEEN THE ELECTRON GAS METHOD AND THE
MOLECULAR ORBITAL METHOD

Dear Editor:

It follows from an investigation of the relation between the electron gas method and the method of molecular orbitals that in solving the problem of the π-electrons of a conjugated system of $\underline{n}$ atoms of C by the method of molecular orbitals, the coefficients of linear combinations of the p_c functions can be found in the simplest form with the help of the first $\underline{n}$ solutions of the equation of an electron in a potential trough with a constant potential

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\psi(x) = 0 \qquad (1)$$

under specific boundary conditions. Here we assume that the distances between neighboring C atoms are equal.

Equation (1) may be replaced by the more general equation of the theory of eigenvalues:

$$\frac{d^2\psi(x)}{dx^2} + Ak\psi(x) = 0 \qquad (2)$$

under the same limiting conditions, where A is a parameter which may be varied. It is convenient to link Eq. (2) with a vibrating system in which a certain point $x(C_i)$ corresponds to the $\underline{i}$th atom of C. If the distances between neighboring C atoms are identical, the $\underline{r}$th coefficient of the $\underline{j}$th linear combination of the method of molecular orbitals is equal to the value of the $\underline{j}$th equation (2) at the point $x(C_p)$. When the distances between neighboring C atoms are different, solutions of Eq. (2) lead to approximate values of the coefficients of linear combinations of the p_c functions of the method of molecular orbitals. It can be shown that the difference between $j + 1$ and $\underline{j}$ eigenvalues of Eq. (2) and the difference between $j + 1$ and $\underline{j}$ energy levels of the method of molecular orbitals are approximately the same if we choose an appropriate form of A. Thus, for a linear molecule, these differences are characterized by a value smaller than $\dfrac{\pi^4}{12} |\beta| \dfrac{|2j + 1| |2j^2 + 2j + 1|}{|n + 1|^4}$, , if we select $A = -\dfrac{1}{\beta}$, where β is the resonance integral. Hence we see that these differences are distinguished by a small fraction of $|\beta|$ with sufficiently large values of $\underline{n}$ (the smaller the magnitude of $\underline{j}$ the smaller the fraction of $|\beta|$). On putting $A = \dfrac{\hbar^2}{2m}$, we obtain Eq. (1).

D. A. Bochvar, I. V. Stankevich and A. L. Chistyakov

CLEAVAGE OF ORGANOSILOXANES BY HALOSILANES

Dear Editor:

We have found that the siloxane bond in organosiloxanes is cleaved by organohalosilanes according to the general scheme (1):

$$R_3SiOSiR_3 + R'_3SiX \rightleftarrows R_3SiOSiR'_3 + R_3SiX, \tag{1}$$
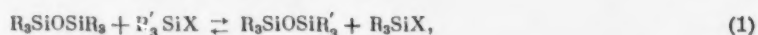
in which X is halogen, R and R' are identical or different organic or siliconorganic radicals, H, halogen, etc.; R is usually different from R'. This reaction, which is often reversible, is catalyzed by metallic halides which are Lewis acids, for example, $FeCl_3$. It is carried out by simple rectification of a mixture of the starting components to which the catalyst is gradually added in course of distillation. Due to the removal of the lower boiling component, the reaction equilibrium is shifted. This new reaction, affording the possibility of synthesizing a whole series of diverse organosiloxanes, may be utilized,for example, in the following syntheses:

1. Synthesis of hexaorganodisiloxanes according to scheme (1). Reaction of $(C_2H_5)_3SiCl$ with $(CH_3)_6Si_2O$ or with $[CH_3(C_2H_5)_2Si]_2O$ gave a 60-70% yield of $(CH_3)_3SiOSi(C_2H_5)_3$ and $CH_3(C_2H_5)_2SiOSi(C_2H_5)_3$.

2. Transformation of lower hexaorganodisiloxanes into higher ones or of higher trialkylhalosilanes into lower ones according to scheme (2).

$$R_3SiOSiR_3 + 2R'_3SiX \rightarrow R'_3SiOSiR'_3 + 2R_3SiX. \tag{2}$$
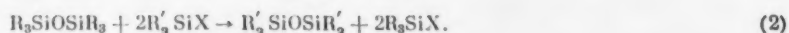
Thus, for example, reaction of $(CH_3)_6Si_2O$ with $(C_2H_5)_3SiCl$ or with $(C_3H_7)_3SiBr$ gives, respectively, $(C_2H_5)_6Si_2O$ (54%) and $(CH_3)_3SiCl$ (75%) or $(C_3H_7)_6Si_2O$ (60%) and $(CH_3)_3SiBr$ (80%).

3. Lengthening of the chain of organosiloxanes according to scheme (3):

$$2R_3SiOSiR_3 + R'_2SiX_2 \rightarrow R_3SiOR'_2OSiR_3 + 2R_3SiX. \tag{3}$$
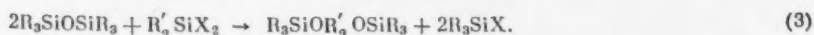
In this manner, for example, we reacted $(CH_3)_6Si_2O$ with $(CH_3)_2SiBr_2$, $(C_2H_5)_2SiCl_2$ and $C_2H_5SiHCl_2$ and obtained the trisiloxanes corresponding to scheme (3) in yields of 75, 54 and 35%, respectively.

Other possibilities of this reaction and further detailed information will be published later.

M. G. Voronkov and L. M. Chudesova

ERRATA

In the issue of 1957, No. 10, on p 1250, the authors' names should read: V. T. Bykov, V. G. Gerasimova, and N. I. Zalevsky.

CHRONICLE

Under the Chairmanship of Academician A. P. Vinogradov a general meeting of the Division of Chemical Sciences of the Academy of Sciences, USSR was held on May 30-31, 1957. A report on the theme of "spectroscopy of molecular compounds with metallic halides" was submitted by Academician A. N. Terenin. He reported that the observed shifts of the ultraviolet spectrum of unsaturated, aromatic and other molecules on addition of halides of B, Al, Zn, Fe, Sn and Sb do not (for the greater part) permit of unequivocal conclusions about the structural changes occurring in the molecules as the result of such additions. The following causes of the observed spectroscopic effects are put forward as possibilities: a) migration of electrons; b) formation of ionic radicals; c) intramolecular electron transfer.

Plotting of vibration spectra of molecular compounds is a promising method. Infrared spectra of these compounds have barely been studied. In work by the reporter and V. N. Filimonov and student D. Borozov at the Leningrad State University, molecular compounds of some simple inorganic and organic molecules with $AlCl_3$, $AlBr_3$ and $SnCl_4$ were investigated. The usual procedure employed in this work was sorption of the vapor of the compound by sublimed films of the halide in high vacuum in the absence of extraneous solvent.

The reporter noted the following among the results obtained: 1) sharp rise in frequency of vibration of NO (the exact effect depending upon the halide) which testifies to the partial ionization on entry into the compound; in the NO^+ ion the frequency of the valence vibration is higher than in the neutral molecule; increased frequency of vibration of the CN group in acetonitrile, analogous with (but greater in magnitude than) that observed on addition of protonic acids; 3) change of frequencies of the pyridine ring, bringing them closer to the frequencies of the benzene ring; 4) sharp fall in the frequency of the $C=C$ bond of cyclohexene without appreciable changes of the remaining frequencies of the ring; 5) sharp change of the frequency of the carbonyl group in acetone, indicating transformation of the bond from a double bond into a one-and-a-half bond; 6) shift of the frequencies of the $C-H$ of diethyl ether in a manner entirely similar to that observed in oxonium compounds; 7) decrease of the frequency of $O-H$ and $C-O$ in methanol with simultaneous increase of the $C-H$ frequency. All these changes, A. N. Terenin said, directly illustrate the strong electron-accepting character of the halides in question and enable us to localize the site of their addition. The resultant molecular compounds can be regarded as intermediate complexes which condition the molecule to the rearrangement of bonds observed on subsequent catalytic transformation.

The Raman spectra of monocrystals of molecular compounds of $SbCl_3$ and $SnCl_4$ with a series of benzene derivatives, which were investigated in the same laboratory at Leningrad State University by Sh. Sh. Raskin, reveal shifts and resolutions of the frequencies of the valence vibrations of the halides entering into combination. Other investigators have already described analogous phenomena, but for liquid solutions. Out of the results obtained, the following may be singled out for mention: the decrease and splitting of the frequency of the $C=O$ bond of benzaldehyde into components on entering into combination with $SbCl_3$, and also the small but perfectly definite lowering of the $C-C$ frequency of the benzene ring in molecular compounds of benzene, toluene and p-xylene with the same agent.

The following took part in the discussion on the report: Corresponding Member S. Z. Roginsky, Corresponding Member B. V. Nekrasov, Doctor of Chemical Sciences N. D. Sokolov, Corresponding Member M. M. Shemyakin, Doctor of Phys.-Math. Sciences A. I. Kitaigorodsky, Academician A. P. Vinogradov.

Corresponding Member of the Academy of Sciences, USSR B. P. Nikolsy (co-authors M. M. Shults and N. P. Isakova) presented a report on the theme of "influence of the composition of boroaluminosilicate glasses on their electrode and acidic properties." It was reported that an ion-exchange reaction occurs when a sodium glass comes into contact with a solution:

$$Na^+ (glass) + H^+ (aqueous\ solution) = Na^+ (aqueous\ solution) + H^+ (glass).$$
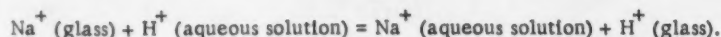
The velocity constant of this heterogeneous reaction characterizes the relative "affinity to glass" of hydrogen ions and sodium ions, as well as the acidic and electrode properties of a glass. Introduction of boron trioxide or alumina into the glass shifts the equilibrium of the above ion-exchange reaction to the left, while increase of content of oxides of the alkali and alkaline earth metals shifts it to the right. This signifies that with increasing content of boron trioxide or alumina in the glass, the equilibrium constant (exchange constant) is increased, while with increasing content of oxides of sodium and calcium it is decreased. The relation between the exchange constant and the composition of glasses is therefore a complex one.

This relation is considerably simplified, however, if we take into account the chemical role of all these oxides in a glass. Oxides of sodium and calcium are the basic components of glasses, and oxides of silicon, boron and aluminum are acidic. Interaction of silica with basic oxides gives salts of a weak acid (simple silicates), while reaction of boron trioxide and alumina with excess of silica and with basic oxides gives salts of strong acids (boro- and aluminosilicates). Since the exchange constant serves as a general characteristic of the acid properties of a glass, it is natural to expect that its magnitude must govern the ratio in a glass of the salts of weak and strong acids. Indeed, on a log K versus X diagram, the points for all of 19 investigated boro- and aluminosilicate glasses fit satisfactorily on one smooth parabolic curve, i. e., the exchange constant is a unique function of the acidity ratio X. It therefore follows, said B. P. Nikolsky, that the hydrogen function of the glass electrode is associated with the weak acidic properties of glasses; in other words, with a small value of the exchange constant K the hydrogen function ought to be manifested in advance of the sodium function in glasses containing a small proportion of boron trioxide and alumina as compared with glasses containing oxides of sodium and calcium; this is fully confirmed by experiment. Conversely, the sodium electrode function will be preferentially manifested in glasses rich in boron trioxide and alumina and poor in bases, and this is consistent also with experiment. The relation between the exchange constant and the weak acid/strong acid ratio in glasses can be easily expressed in a rectilinear form. This rectilinear relation must be regarded as semiempirical.

Academician V. A. Kargin and Corresponding Member N. I. Nikitin took part in the discussion on the report.

Ya. I. Ryskin (Institute of Silicate Chemistry of the Academy of Sciences, USSR) gave a report on the theme of "the hydrogen bond in silicon compounds with reference to infrared spectrometric data." The reporter spoke of the influence of the hydrogen bond on the skeletal vibrations of alkyl- and arylsilanes. He obtained (in the 400-4000 cm^{-1} region) the absorption spectra of six alkyl- and arylsilanes and silanediols in the associated molecular state and also in the nonassociated state (in solutions). The reporter commented on the untenability of the attempts at interpretation of the spectra of silanols described in the literature. Development of a hydrogen bond between molecules of silanols is accompanied by resolution of band I γ (Si—OH) into two equally intense components and by shift of the center of gravity of the double band toward higher frequencies (by approximately 20 cm^{-1}).

The hydrogen bond between molecules of a silanol and an "active" solvent (pyridine, dioxan , methyl ethyl ketone, acetone) leads to an increase in the vibration frequency of I ($\Delta \nu \sim 50$ cm^{-1}), but in this case there is no resolution of the absorption band. This is also to be expected, since different molecules are linked and the conditions for resonance vibration are absent. Investigation of the spectra of triethylsilanol and deuterotriethylsilanol enabled the frequencies of the deformation vibrations of the hydroxyl to be determined. The influence of the hydrogen bond upon the corresponding absorption bands will be the subject of later investigations by the reporter.

M. A. Porai-Koshits, Corresponding Member, A. D. Petrov and others took part in the discussion on the report.

Doctor of Phys.-Math. Sciences A. I. Kitaigorodsky submitted a report on the theme of "conditions of formation of solid solutions of organic compounds." A distinguishing feature of organic crystallochemistry, said the reporter, is that the categories of symmetry and close packing are found to be fully adequate for the understanding

of the structure of an organic crystal. This is by no means true of metallic and inorganic crystals in which the intraatomic electron bonds can completely suppress the factors of symmetry and close packing. For this reason, an attempt was made to formulate a law of formation of solid solutions for organic substances. In the opinion of the reporter, solid substitution solutions are mainly of interest in organic crystals. A foreign molecule is capable of replacing a molecule of the substrate crystal if the molecules of both types are similar in shape and size. Similarity of size of atoms in inorganic and metallic crystals is a necessary condition for formation of solid substitution solutions. In organic crystals the condition of similarity of shape and size is necessary and sufficient. If substitution can be effected with approximately the same number of contacts and with retention of the intramolecular radii within the permissible limits, then solid solutions are formed on displacement. Solid substitution solutions of organic compounds are also possible with an inorganic solvent. For the formation of such solutions, however, isomorphism of the molecules is only a necessary condition but not a sufficient condition.

The reporter commented that a continuous series of solid solutions is only possible when: a) the symmetry of arrangement of molecules in mixed crystals is uniform; b) with differing symmetry of the mixed crystals, the molecules of one of the components are nonsymmetrical. The reporter is aware of examples of organic substances in which not only are the molecules very similar in shape and size but the packings of the molecules are also very similar. A continuous series of solid solutions becomes impossible, however, if this similarity is accompanied by a difference in the symmetry of mutual arrangement of the molecules. Insolubility must develop in a certain range of concentrations; in other words, a continuous change of concentration in the solid state is only possible through phase transition. Consequently, up to a certain percentage content, molecules of B are accommodated in a crystal lattice of A; at the other end of the phase diagram, crystals of solid solution are formed in which molecules of A are accommodated in the crystal lattice. The more similar the molecules of such crystals are in shape, and the closer the resemblance between the packing systems, the narrower must become the interval in which solubility disappears. Therefore, in the opinion of A. I. Kitaigorodsky, it is not surprising that investigators have not detected this break in solubility and have found a continuous series of solid solutions in cases where the continuity was actually broken. The ideas formulated by the reporter were verified by a study of the systems anthracene—phenanthrene, stilbene—dibenzyl and anthracene—acridine. All of these systems were formerly described as series of continuous solid solutions. According to the theory here enunicated, these systems must possess discontinuous solubility.

The following participated in the discussion on the report: Corresponding Member of the Academy of Sciences, USSR B. V. Nekrasov, Doctor of Chemical Sciences E. S. Makarov, V. G. Kuznetsov and Corresponding Member of the Academy of Sciences, USSR S. Z. Roginsky.

Doctor of Chemical Sciences M. M. Koton (co-author Yu. V. Mitin) reported on the theme of "synthesis of polymers with rings in the chains." The reporter pointed to the scientific and practical interest in polymers containing various aromatic and heterocyclic radicals in an ethylene molecule. He gave an account of formation of polymers made up from rigid cyclic segments: polyphenylenes, terfluoropolyphenyls, polymers of 2,3-dihydrofurfural, polyacenaphthylene. M. M. Koton pointed also to the possibility of preparation of new polymers with cyclic segments on the basis of hydrocarbons containing two isopropenyl groups, and he reported on routes for synthesis and on the properties of these hydrocarbons; he also discussed the structure and properties of the polymers obtained, the influence of the polymerization conditions on the formation of soluble linear or insoluble crosslinked polymers. M. M. Koton's report was followed by numerous question.

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A meeting of the Division of Chemical Sciences of the Academy of Sciences, USSR was held on June 28, 1957 under the Chairmanship of Academician N. N. Semenov to mark the 50th birthday of Academician Valentin Alekseevich Kargin.

Academician V. A. Kargin reported on the theme of "structure and phase structure of polymers." He pointed out that any structural investigation resolves itself into a problem of determination of the molecules and molecular groups or atoms from which the molecules of the investigated substance are made up. With very large dimensions of polymer molecules, the usual structural methods are suitable only for determination of the position of individual molecular groups, while we must resort to other methods (electron microscopy in the first place) for evaluation of the orientation of the molecules. A high degree of order may be attained in polymers, the reporter said, by

two methods: by crystallization of the polymer or by mutual orientation of chain molecules resulting from deformation and (especially) flow of polymers. Cellulose is an example of such a highly ordered but amorphous polymer. Its lack of crystallinity can be demonstrated by structural and thermodynamic methods. Alteration of the degree of order, resulting from orientation and crystallization of polymers, is a constant source of misunderstandings in the evaluation of the phase condition of polymers.

Chain molecules consist of identical, regularly arranged molecular groups, and a cluster of chains in parallel arrangement is itself a well-ordered structure. Crystallization increases this ordered arrangement even more in that the chains are regularly arranged with respect to one another. It is necessary to differentiate between ordered arrangement created by a regular structure of the chains and that developed on crystallization. This can be done by x-ray or electron-microscopic examination of crystallizing polymers at temperatures above and below the melting point of the polymer crystals. A second method is the investigation of the structure of highly oriented polymers at temperatures above and below the crystallization temperature while retaining the orientation of the polymer unchanged. These investigations revealed the existence of a high degree of order in a series of amorphous polymers, and they led to the hypothesis that good, mutual regularity of chain molecules can even be developed in the amorphous state and is a necessary but not sufficient condition for crystallization of polymers.

In electron-microscopic examinations we usually see not the individual crystals but the so-called spherolites; the latter are usually regarded as aggregates of small crystals. It can be shown, however (V. A. Kargin said), that spherolites remain intact when crystallites are broken down under the action of high-energy radiations. On the other hand, spherolites can be completely broken down by mechanical treatment without the crystallinity of the polymer being altered. Consequently, it may be suggested that spherolites are not intergrowths of crystals but are developed by irregular change of density during crystallization. Observations on thin oriented films may reveal resolution of the polymer into clusters of fine filaments in which small periodic thickenings occur during crystallization. These thickenings can presumably be described as unit crystallites of the crystal polymers. Resolution into thin clusters, each containing several dozens of chains, can sometimes be observed also in amorphous polymers. Thus, the electron-microscopic examination confirms the possibility of effective reciprocal orientation of chains in amorphous polymers as a necessary prerequisite of crystallization.

On evaporating very dilute solutions of polymers on supports, individual molecules can be observed under the electron microscope, and the formation of aggregates from them can be followed. Observations on a series of water-soluble polymers showed that chain molecules either roll up into entities of nearly spherical shape or unwind into straight chains. In the former case the spherical globules aggregate like ordinary colloidal particles — without mutual penetration. The coiled chains collect in aggregates each containing some dozens of chains. We can thus observe the formation of structures in polymers on transition from individual molecules to ever more complex aggregates. At the same time we can observe the development of ordered structures in amorphous polymers. All this confirms the general conclusion that crystallization of polymers is only the last step in processes of mutual ordering of chains which take place within the limits of the amorphous state of polymers and which must not be confused with phase transformations.

G. L. Slonimsky (co-authors T. I. Sogolova and V. A. Kargin) reported on the theme of "flow characteristics of polymers." Viscous flow of amorphous, linear polymers, the reporter said, is developed by heating and occurs in a narrow temperature range which is the higher the greater the degree of polymerization. The main features differentiating the flow of linear, amorphous polymers from the flow of low-molecular liquids are the unavoidable development of large reversible deformations of the flowing polymer and the nondependence of the activation energy of viscous flow on the degree of polymerization. These characteristic differences, due to the flexibility of the long chains of polymer molecules, govern the special features of formation from polymers of fibers, films and massive elastic and solid articles. Deviation of the behavior of a flowing polymer from the behavior of a Newtonian viscous liquid is caused by the change of shape of polymer molecules during viscous flow. The law of flow of polymers can be established only by taking into account the reciprocal influence of the processes of development of reversible (elastic) and nonreversible deformations. Application of large mechanical stresses leads to rupture of the chemical bonds in chain molecules with formation of free radicals, due to which the lability of the structural elements of the polymer is sharply increased. In this case, the reporter said, the normal flow of polymers has superposed on it a process of flow resulting from transfer of the mechanical stresses to portions of the chain molecules, and this process is accompanied by the chemical process of structure formation (free-radical interaction). This type of polymer flow may be called chemical flow. Three-dimensional polymers, in which

normal flow is impossible, can be subjected to shaping operations under conditions of chemical flow with the help of rapid applications of sufficiently high mechanical stresses. The free-radical mechanism of chemical flow opens up wide possibilities of chemical control of changes of properties of polymers in the course of their technological processing by introduction into the polymer of inhibiting and initiating additives and various monomers.

Doctor of Chemical Sciences N. V. Mikhailov (co-authors V. I. Maiboroda and V. A. Kargin) presented a report on the theme of "a new method of production of viscose fiber." The chemical feature of the new method the reporter said, is the inclusion of sodium bicarbonate with the sodium hydroxide in the viscose solutions, the precipitation of cellulose xanthate from the solutions, and hydrolysis of the xanthate in an alkaline medium. Technical stages in preparation of fiber by the new method are: 1) formation of xanthated fiber in baths containing $NaHCO_3$ and Na_2SO_4; 2) decomposition of cellulose xanthate and regeneration of the hydrated cellulose fiber in an alkaline medium at 130-150°; 3) regeneration of the starting components (NaOH and $NaHCO_3$) and hydrolysis of secondary products with conversion of the CS_2 into free H_2S (employing carbonation with carbon dioxide gas) and later oxidation of H_2S to S. The chemical scheme of the new method, the reporter said, ensures innocuousness of the process of viscose fiber manufacture at all stages of its formation and finishing, enables fiber to be produced without sulfuric acid and zinc sulfate, affords the possibility of utilization of carbon dioxide from flue gases, reduces the consumption of chemical raw materials, and simplifies the technological process. Regeneration of NaOH, $NaHCO_3$, sulfur and other chemical products and the items of equipment are similar to those in the soda industry and the corresponding branches of the coke-chemical industry. Utilization of carbon dioxide from flue gases and the possibility of using waste gases in the ammonia industry increases the over-all value of the new method of manufacture of viscose staple fiber. Results of laboratory investigations were checked in 1956 on an experimental plant producing standard-quality staple fiber. The physicomechanical properties of the latter satisfied the requirements of the textile-processing industry. Viscose fiber produced by the new alkaline method, the reporter said, differs from fiber produced by the acid method by its structural homogeneity, by its nonshrinkage, and by the higher density of its molecular packing.

Prof. V. I. Sharikov, Corresponding Member S. Z. Roginsky and Doctor of Chemical Sciences V. I. Ivanov participated in the discussion on the report. Greetings were conveyed to Academician V. A. Kargin by Academician N. N. Semenov, D. P. Novikov (on behalf of the Minister of Chemical Industry), Prof. V. I. Veselovsky, Corresponding Member Ya. I. Gerasimov, Academician P. A. Rebinder and Prof. E. O. Kuvshinsky.

Bulletin of the Academy of Sciences of the USSR

Division of Chemical Sciences

IN ENGLISH TRANSLATION

November 1957

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

August 15, 1958

Mr. Earl Coleman
Consultants Bureau
227 West 17th Street
New York 11, New York

Dear Earl:

Now that we are about to renew our contract for another year for translated issues of Biochemistry and Bulletin of Experimental Biology and Medicine, it seems appropriate to review the performance of Consultants Bureau over the past year. This is even more pertinent because the circumstances under which we procure these translations from your firm differs from those under which we contract for the publication of other journals. Since these two translated journals were started at your initiative, and are the property of Consultants Bureau, your firm has complete independence in the matter of translation quality and speed of publication.

In distributing these two journals to 400 medical research libraries we have exposed them to the white light of publicity before a highly critical scientific community. We have yet to receive a single letter critical of the translations made by your firm. To the contrary, we have been receiving a number of letters from medical scientists, and their spokesmen, the medical libraries, throughout the country, reporting how highly thought of these journals are in the scientific community. This speaks volumes for the high standards of translation and editing which you have established and maintained.

We are equally pleased with the speed of delivery of these translated journals. I am well aware of the tremendous strains on your production staff occasioned by the sharp accumulations of pressures for the translation of Russian science and technology. The fact that your staff has been able to maintain its translation and publication schedules, and produce these and the other journals on your program without interruption during these critical months is indeed a cause for congratulations.

On our part, we are gratified both with your product, and with the contribution it has made to the advancement of medical research in the United States. We are placing this renewal order with you in full confidence that the future issues of these two translated journals will maintain the high standards you have set for yourself.

Sincerely yours,

Scott Adams

Scott Adams, Librarian
National Institutes of Health